

# Chemistry—A European Journal

## Supporting Information

### Photoinduced and Thermal Single-Electron Transfer to Generate Radicals from Frustrated Lewis Pairs

Flip Holtrop,<sup>[a]</sup> Andrew R. Jupp,<sup>[a]</sup> Nicolaas P. van Leest,<sup>[a]</sup> Maximilian Paradiz Dominguez,<sup>[a]</sup> René M. Williams,<sup>[a]</sup> Albert M. Brouwer,<sup>[a]</sup> Bas de Bruin,<sup>[a]</sup> Andreas W. Ehlers,<sup>[a, b]</sup> and J. Chris Slootweg<sup>\*[a]</sup>

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**SUPPORTING INFORMATION****1. Experimental Procedures****General considerations**

All manipulations regarding the preparation of air-sensitive compounds were carried out under an atmosphere of dry nitrogen using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures. The EPR spectra were recorded on a Bruker EMX X-band spectrometer and further analyzed and simulated using the W95EPR program of Prof. F. Neese. UV/Vis absorption spectra were recorded using a Shimadzu UV-2700 spectrophotometer. Tris(3,5-dinitromesityl)borane was obtained from trimesitylborane via literature procedure.<sup>1</sup> The following reagents were purchased from commercial sources: BCF (>98%, TCI chemicals), PMes<sub>3</sub> (97%, Sigma Aldrich), PtBu<sub>3</sub> (98%, Sigma Aldrich), Np-Tol<sub>3</sub> (>98.0%, TCI chemicals), NPh<sub>3</sub> (>99% Acros Organics), [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (97%, Alfa Aesar) and used without further purification.

**2. Computational details: Ionization potentials and electron affinities**

All structures in this section were optimized at the ωB97X-D/6-31G(d) level of theory after which single point calculations were performed using the 6-311+G(d,p) level in combination with different functionals (ωB97X-D and M06-2X, of which the latter was used for direct comparison with the work of Müller *et al.*) (See Table S1)<sup>2,3,4</sup> using Gaussian 09, Revision D01.<sup>5</sup> Solvent was taken into account where specified by applying Self-Consistent Reaction Field (SCRF) method using the polarizable continuum model. The table show that values obtained using the ωB97X-D and M06-2X functionals are similar, resulting in the same trends and conclusions. In the paper we refer to the ωB97X-D/6-311+G(d,p) with a solvent correction for toluene as this is most relevant for our experimental work which was mostly performed in this solvent.

**Table S1.** Ionization potentials and electron affinities for different donors and acceptors calculating using different functionals and PCM solvent corrections

Functional	ωB97X-D	ωB97X-D	ωB97X-D	M06-2X	M06-2X
Solvent	None	toluene	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>5</sub> Cl	None
<b>Ionization potentials</b>					
PMes <sub>3</sub>	6.29	5.54	5.25	5.38	6.42
PtBu <sub>3</sub>	6.93	5.95	5.55	5.62	6.99
NPh <sub>3</sub>	6.81	5.94	5.59	5.74	6.95
NpTol <sub>3</sub>	6.46	5.67	5.35	5.49	6.60
N <sup>b</sup> Ar <sub>3</sub>	6.46	5.67	5.36	5.51	6.60
<b>Electron affinities</b>					
BCF	-2.31	-3.03	-3.31	-3.59	-2.59
B(NO <sub>2</sub> -Mes) <sub>3</sub>	-2.55	-3.04	-3.22	-3.51	-2.83
CPh <sub>3</sub> <sup>+</sup>	-6.09	-5.23	-4.89	-4.94	-6.15

ΔE in eV

## SUPPORTING INFORMATION

**Table S2.** Energy differences between electron donor-acceptor pair (D + A) and their corresponding radical ion pairs ( $D^{+·} + A^{-·}$ ) calculated using different functionals and PCM solvent corrections

Functional		$\omega$ B97X-D	$\omega$ B97X-D	$\omega$ B97X-D	M06-2X	M06-2X
Solvent		None	toluene	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>5</sub> Cl	None
BCF	PMes <sub>3</sub>	91.3	57.8	44.35	41.33	88.12
	PtBu <sub>3</sub>	106.0	67.2	51.30	46.59	101.28
	NPh <sub>3</sub>	103.3	67.1	52.25	49.41	100.23
	NpTol <sub>3</sub>	95.3	60.7	46.67	43.72	92.12
	N <sup>b</sup> Ar <sub>3</sub>	95.2	60.8	46.88	44.14	92.15
B(NO <sub>2</sub> -Mes) <sub>3</sub>	PMes <sub>3</sub>	86.1	57.6	46.53	43.25	82.63
	PtBu <sub>3</sub>	100.8	67.2	53.47	48.51	95.79
	NPh <sub>3</sub>	98.1	67.1	54.43	51.33	94.75
	NpTol <sub>3</sub>	90.1	60.5	48.84	45.64	86.63
CPh <sub>3</sub> <sup>+</sup>	PMes <sub>3</sub>	4.4	7.0	8.28	10.13	6.31
	PtBu <sub>3</sub>	19.1	16.4	15.22	15.39	19.48
	NPh <sub>3</sub>	16.4	16.3	16.17	18.21	18.44
	NpTol <sub>3</sub>	8.4	10.0	10.80	12.52	10.32

$\Delta E$  in kcal/mol

## SUPPORTING INFORMATION

**Table S3.** Energy differences between FRP and FLP for selected donor and acceptor combinations and corresponding EPR observations

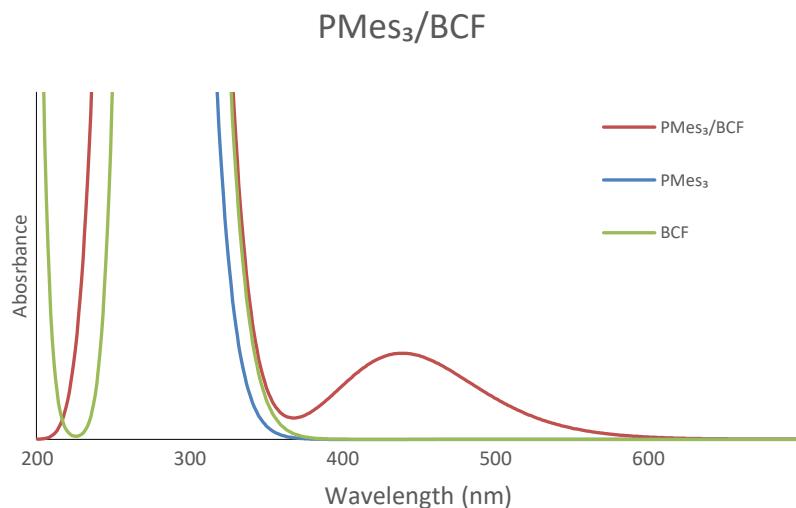
Acceptor	<i>EA<sub>A</sub></i>	Donor	<i>I<sub>b</sub></i>	ΔE	Stability D <sup>[a]</sup>	Stability A <sup>[a]</sup>	SET	Observed	Temp.
BCF	-3.03	PMes <sub>3</sub>	5.54	57.8	unstable	persistent	hv	PMes <sub>3</sub> <sup>•+</sup> and BCF <sup>•-</sup>	30 K
		PtBu <sub>3</sub>	5.95	67.2	unstable	unstable	hv	PtBu <sub>3</sub> <sup>•+</sup> and BCF <sup>•-</sup>	30 K
		NPh <sub>3</sub>	5.94	67.1	unstable	persistent	hv	NPh <sub>3</sub> <sup>•+</sup>	r.t
		NpTol <sub>3</sub>	5.67	60.7	unstable	persistent	hv	NpTol <sub>3</sub> <sup>•+</sup>	r.t
		N <sup>b</sup> Ar <sub>3</sub>	5.67	60.8	unstable	persistent <sup>[g]</sup>	hv <sup>[f]</sup>	N <sup>b</sup> Ar <sub>3</sub> <sup>•+</sup>	r.t
B(NO <sub>2</sub> -Mes) <sub>3</sub>	-3.04	PMes <sub>3</sub>	5.54	57.6	persistent	persistent	hv	None <sup>[d]</sup>	
		PtBu <sub>3</sub>	5.95	67.2	persistent	unstable	hv	B(NO <sub>2</sub> -Mes) <sub>3</sub> <sup>•-</sup>	r.t
		NPh <sub>3</sub>	5.94	67.1	persistent	persistent	hv <sup>[e]</sup>	None <sup>[e]</sup>	
		NpTol <sub>3</sub>	5.67	60.5	persistent	persistent	hv <sup>[e]</sup>	None <sup>[e]</sup>	
CPh <sub>3</sub> <sup>+</sup>	-5.24	PMes <sub>3</sub>	5.54	7.0	persistent <sup>[b]</sup>	persistent	Δ	PMes <sub>3</sub> <sup>•+</sup> and CPh <sub>3</sub> <sup>•</sup>	r.t
		PtBu <sub>3</sub>	5.95	16.4	persistent <sup>[b]</sup>	unstable	Δ	CPh <sub>3</sub> <sup>•</sup>	r.t
		NPh <sub>3</sub>	5.94	16.3	persistent <sup>[b]</sup>	persistent	Δ	NPh <sub>3</sub> <sup>•+</sup>	r.t
		NpTol <sub>3</sub>	5.67	10.0	persistent <sup>[b]</sup>	persistent	Δ	NpTol <sub>3</sub> <sup>•+</sup>	r.t

ΔE in kcal/mol calculated at SCRF/ωB97X-D/6-311+G(d,p) level of theory, solvent: toluene. [a] stability of radical at r.t. in toluene solution [b] Gomberg dimerization occurs [c] EPR at 30 K [d] Radicals react with each other [e] BET is expected to regenerate starting FLP [f] predicted based on the ΔE and results reported by Wang *et al.*<sup>6</sup> [g] stability in DCM

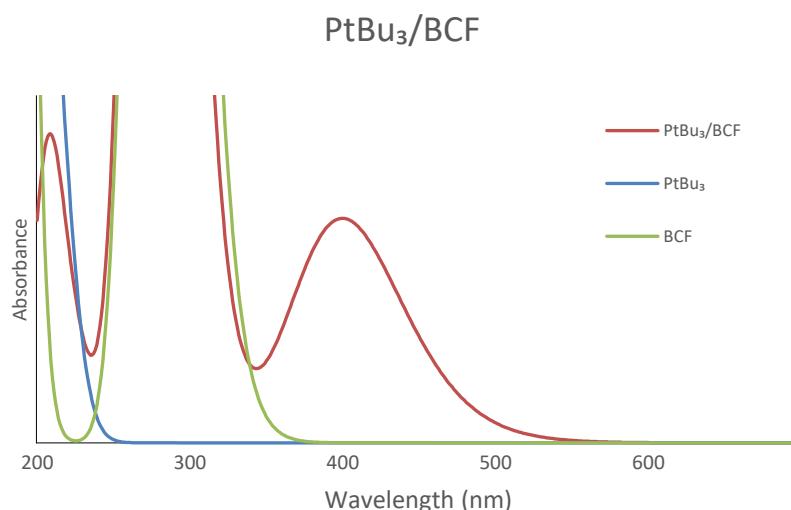
## SUPPORTING INFORMATION

**3. Computational details: Predicted UV-Vis spectra**

All structures in this section were optimized at  $\omega$ B97X-D/6-311G(d,p)<sup>2,3</sup> using Gaussian 09, Revision D01.<sup>5</sup> ZPE and Gibbs free energies ( $G^\circ$ ) were obtained from frequency analyses performed at the same level of theory. Coordinates are given in the last section of this SI. TD-DFT analyses were performed at the  $\omega$ B97X-D/6-311++G(d,p) level of theory. The first 20 vertical excitations were calculated to generate the absorption spectra. As the first states are most relevant, the first 4 are given below. In all cases no solvent was taken into account.

**Calculated absorption spectra (TD-DFT:  $\omega$ B97X-D/6-311++G(d,p))**

**Figure S1:** Calculated absorption spectra for PMes<sub>3</sub>/BCF and the separate components



**Figure S2:** Calculated absorption spectra for PtBu<sub>3</sub>/BCF and the separate components

**SUPPORTING INFORMATION****Table S4:** Calculated vertical excitations (first 4) for  $B(C_6F_5)_3$ 

	Wavelength (nm)	Oscillator strength
Excited state 1	393.32	0.0240
Excited state 2	289.24	0.0220
Excited state 3	289.24	0.0218
Excited state 4	281.90	0.2836

**Table S5:** Calculated vertical excitations (first 4) for  $PMes_3$ 

	Wavelength (nm)	Oscillator strength
Excited state 1	279.00	0.2341
Excited state 2	278.91	0.2339
Excited state 3	249.99	0.0000
Excited state 4	249.72	0.0154

**Table S6:** Calculated vertical excitations (first 4) for  $PtBu_3$ 

	Wavelength (nm)	Oscillator strength
Excited state 1	214.09	0.0777
Excited state 2	200.70	0.0675
Excited state 3	200.68	0.0674
Excited state 4	193.87	0.0052

**Table S7:** Calculated vertical excitations (first 4) for  $PMes_3/B(C_6F_5)_3$ 

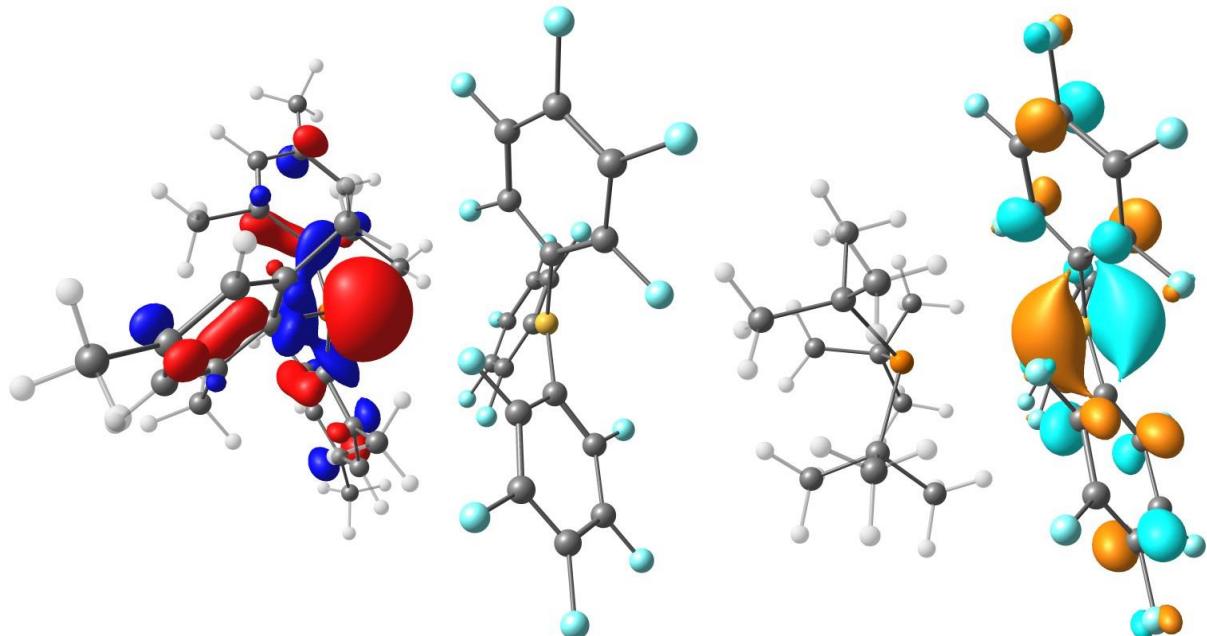
	Wavelength (nm)	Oscillator strength
CT-band	438.96	0.0184
Excited state 2	298.44	0.0235
Excited state 3	293.46	0.0118
Excited state 4	291.76	0.0184

**Table S8:** Calculated vertical excitations (first 4) for  $PtBu_3/B(C_6F_5)_3$ 

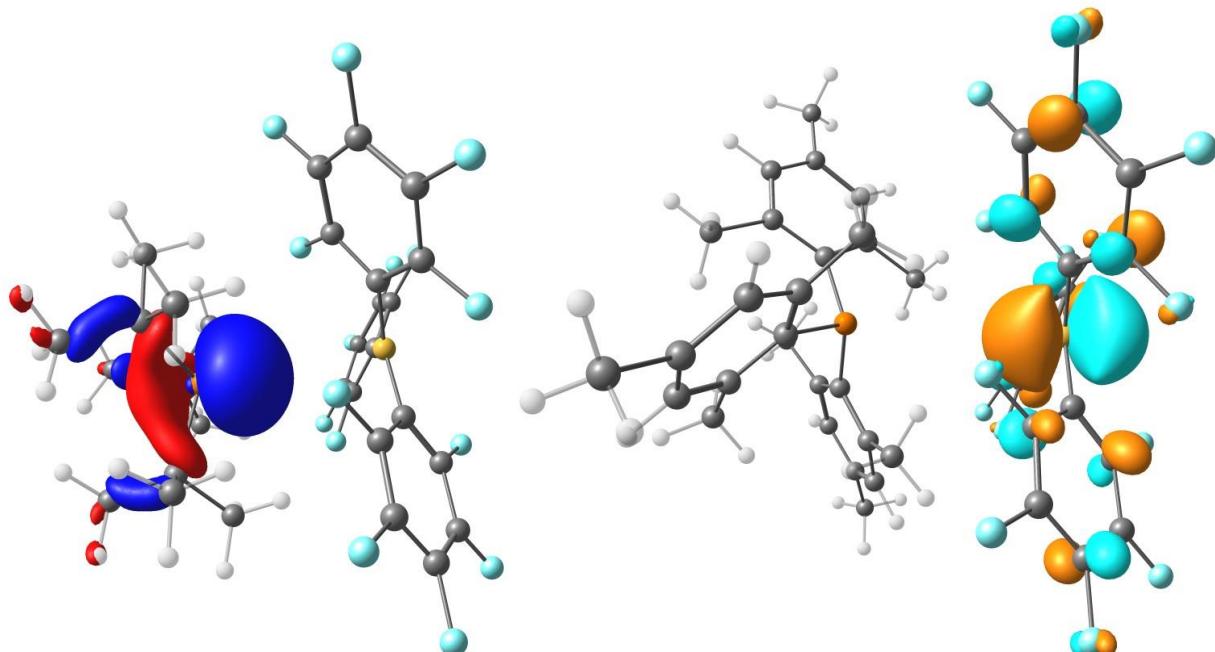
	Wavelength (nm)	Oscillator strength
CT-band	399.84	0.0719
Excited state 2	293.25	0.0279
Excited state 3	286.93	0.0152
Excited state 4	286.92	0.0150

SUPPORTING INFORMATION

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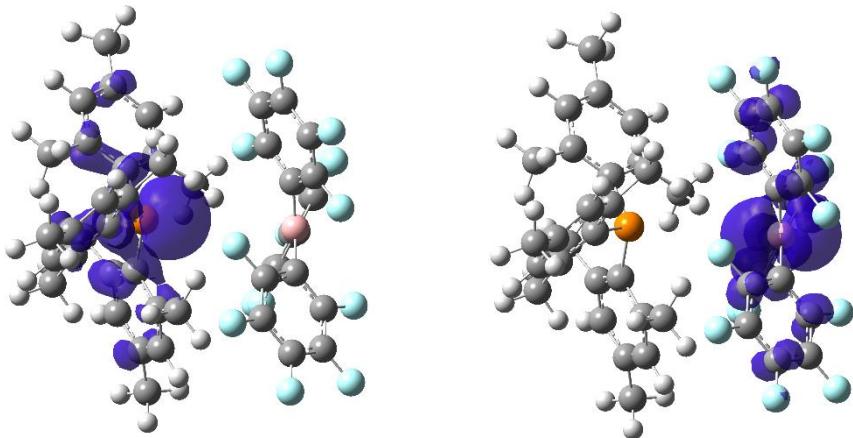


**Figure S3:** Frontier molecular orbitals (HOMO, left, and LUMO, right) of the PMes<sub>3</sub>/BCF encounter complex ( $\omega$ B97X-D/6-311G(d,p))

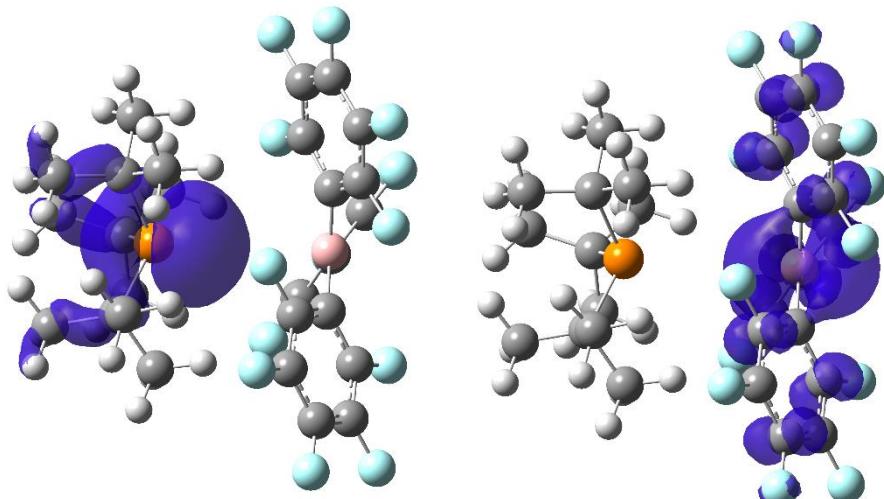


**Figure S4:** Frontier molecular orbitals (HOMO, left, and LUMO, right) of the PBu<sub>3</sub>/BCF encounter complex ( $\omega$ B97X-D/6-311G(d,p))

## SUPPORTING INFORMATION



**Figure S5:** Electron hole (left) and electron density (right) resulting from excitation of the CT-band of  $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ .



**Figure S6:** Electron hole (left) and electron density (right) resulting from excitation of the CT-band of  $\text{PtBu}_3/\text{B}(\text{C}_6\text{F}_5)_3$ .

Orbital contribution to CT-band excitation for  $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ :

# 2 229 -> 230 Coeff.: 0.69422 Contri.: 96.3883%  
# 1 223 -> 230 Coeff.: -0.11022 Contri.: 2.4297%  
229 = HOMO, 2230 = LUMO

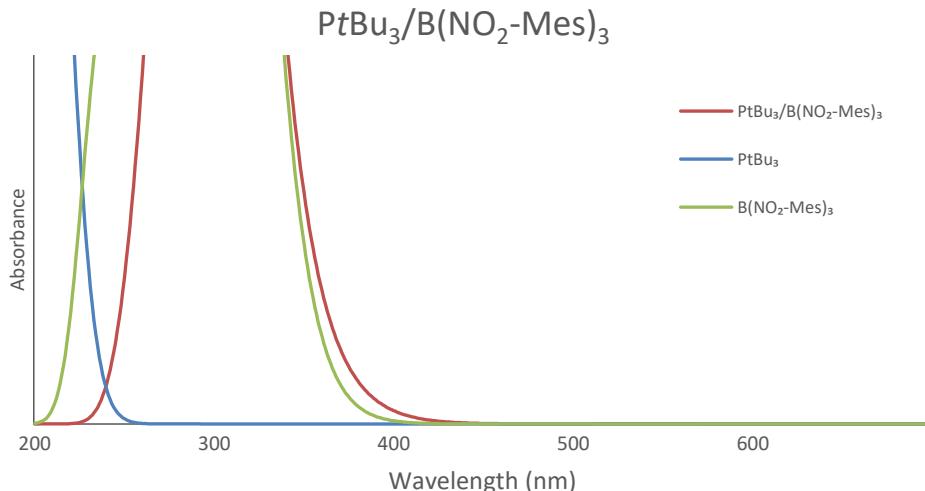
Orbital contribution to CT-band excitation for  $\text{PtBu}_3/\text{B}(\text{C}_6\text{F}_5)_3$ :

# 1 181 -> 182 Coeff.: 0.70158 Contri.: 98.4429%  
181 = HOMO, 182 = LUMO

## SUPPORTING INFORMATION

**Predicted UV-Vis spectra PR<sub>3</sub>/ B(NO<sub>2</sub>-Mes)<sub>3</sub>**

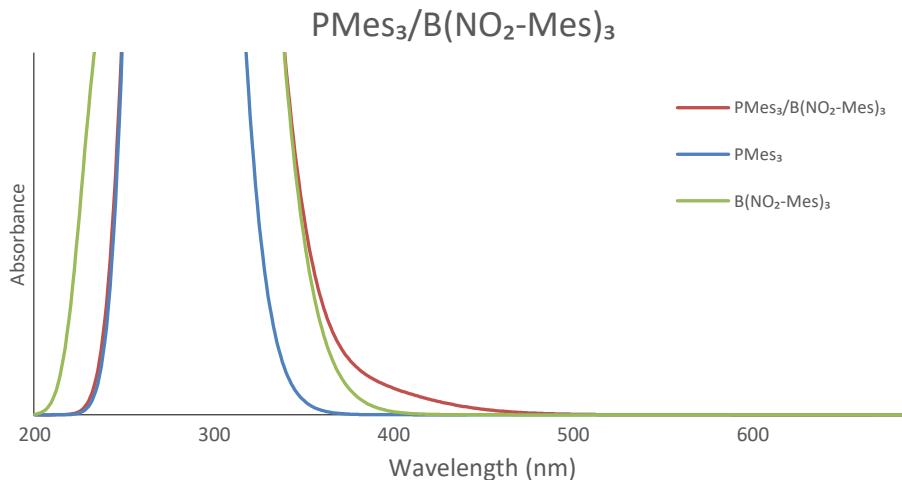
The predicted spectra for these combinations of phosphine and borane do not clearly show the predict CT-band as these lie close to the predicted absorptions for the individual components and are computed to have a low oscillator strength. Therefore, the calculated CT-band and the next 3 absorptions of the P/B combinations are given as well.



**Figure S7:** Calculated absorption spectra for PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> and the separate components

**Table S9:** Calculated vertical excitations for PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub>

	Wavelength (nm)	Oscillator strength
CT-band	342.74	0.0105
Excited state 2	317.18	0.0075
Excited state 3	316.98	0.0075
Excited state 4	316.80	0.0011



**Figure S8:** Calculated absorption spectra for PMes<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> and the separate components

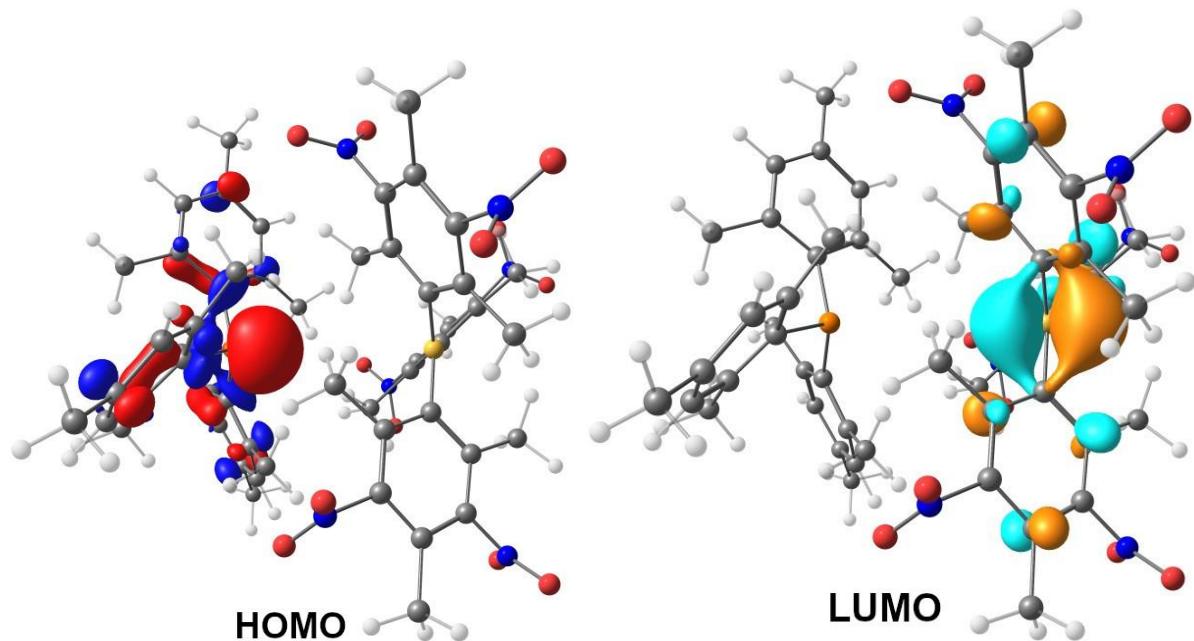
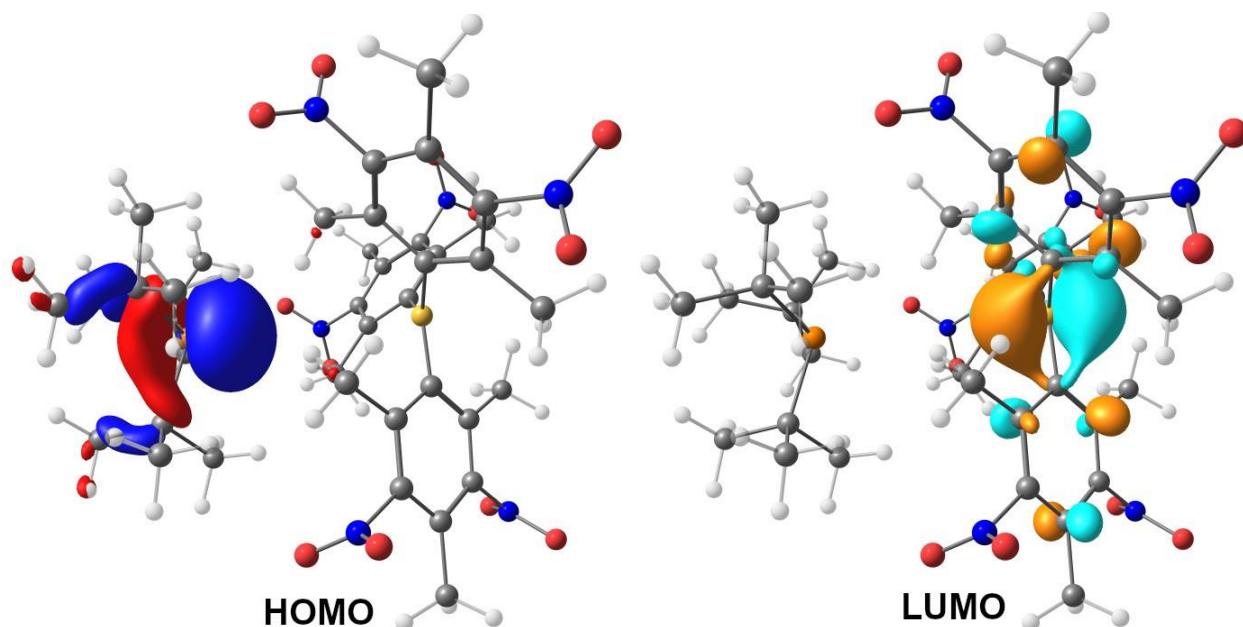
**Table S10:** Calculated vertical excitations for PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub>

	Wavelength (nm)	Oscillator strength
CT-band	380.35	0.0055
Excited state 2	317.56	0.0060
Excited state 3	316.87	0.0104
Excited state 4	316.67	0.0031

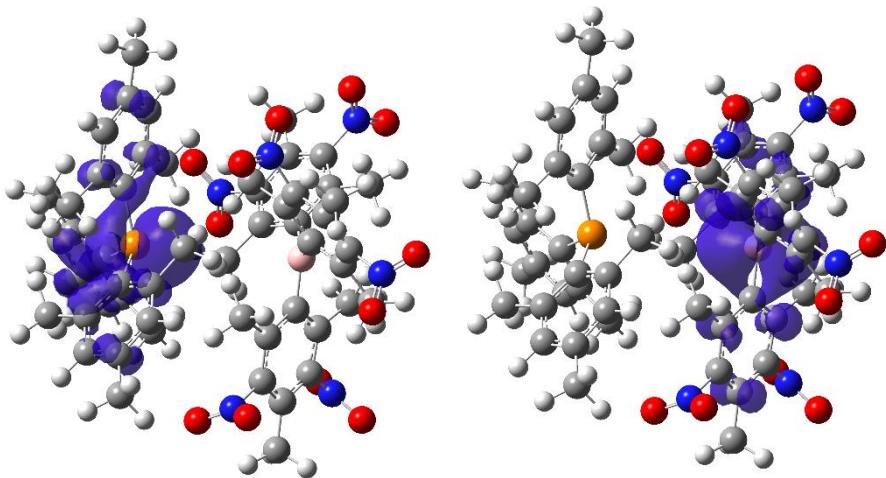
## SUPPORTING INFORMATION

**Table S11:** Calculated vertical excitations for  $\text{B}(\text{NO}_2\text{-Mes})_3$ 

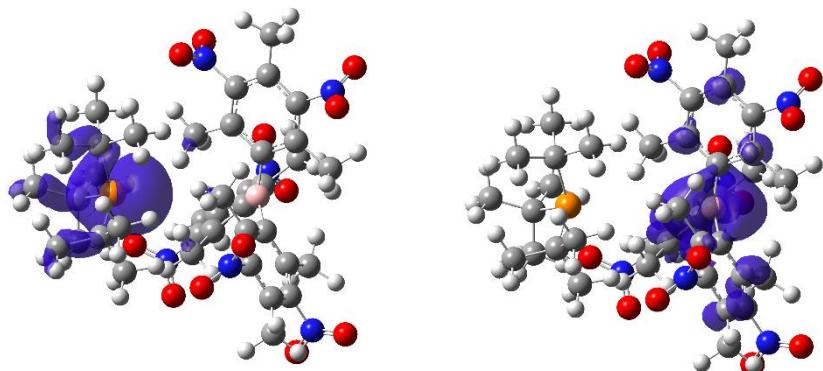
	Wavelength (nm)	Oscillator strength
Excited state 1	315.88	0.0104
Excited state 2	315.87	0.0104
Excited state 3	315.63	0.0001
Excited state 4	313.35	0.0051

**Figure S9:** Frontier molecular orbitals of the  $\text{PMes}_3/\text{B}(\text{NO}_2\text{-Mes})_3$  encounter complex ( $\omega\text{B97X-D}/6-311\text{G}(\text{d},\text{p})$ )**Figure S10:** Frontier molecular orbitals of the  $\text{PtBu}_3/\text{B}(\text{NO}_2\text{-Mes})_3$  encounter complex ( $\omega\text{B97X-D}/6-311\text{G}(\text{d},\text{p})$ ).

## SUPPORTING INFORMATION



**Figure S11:** Electron hole (left) and electron density (right) resulting from excitation of the CT-band of  $\text{PMes}_3/\text{B}(\text{NO}_2\text{-Mes})_3$ .



**Figure S12:** Electron hole (left) and electron density (right) resulting from excitation of the CT-band of  $\text{PtBu}_3/\text{B}(\text{NO}_2\text{-Mes})_3$ .

Orbital contribution to CT-band excitation for  $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ :

# 2 271 -> 272 Coeff.: 0.69310 Contri.: 96.0775%

# 1 265 -> 272 Coeff.: 0.10485 Contri.: 2.1987%

271 = HOMO, 272 = LUMO

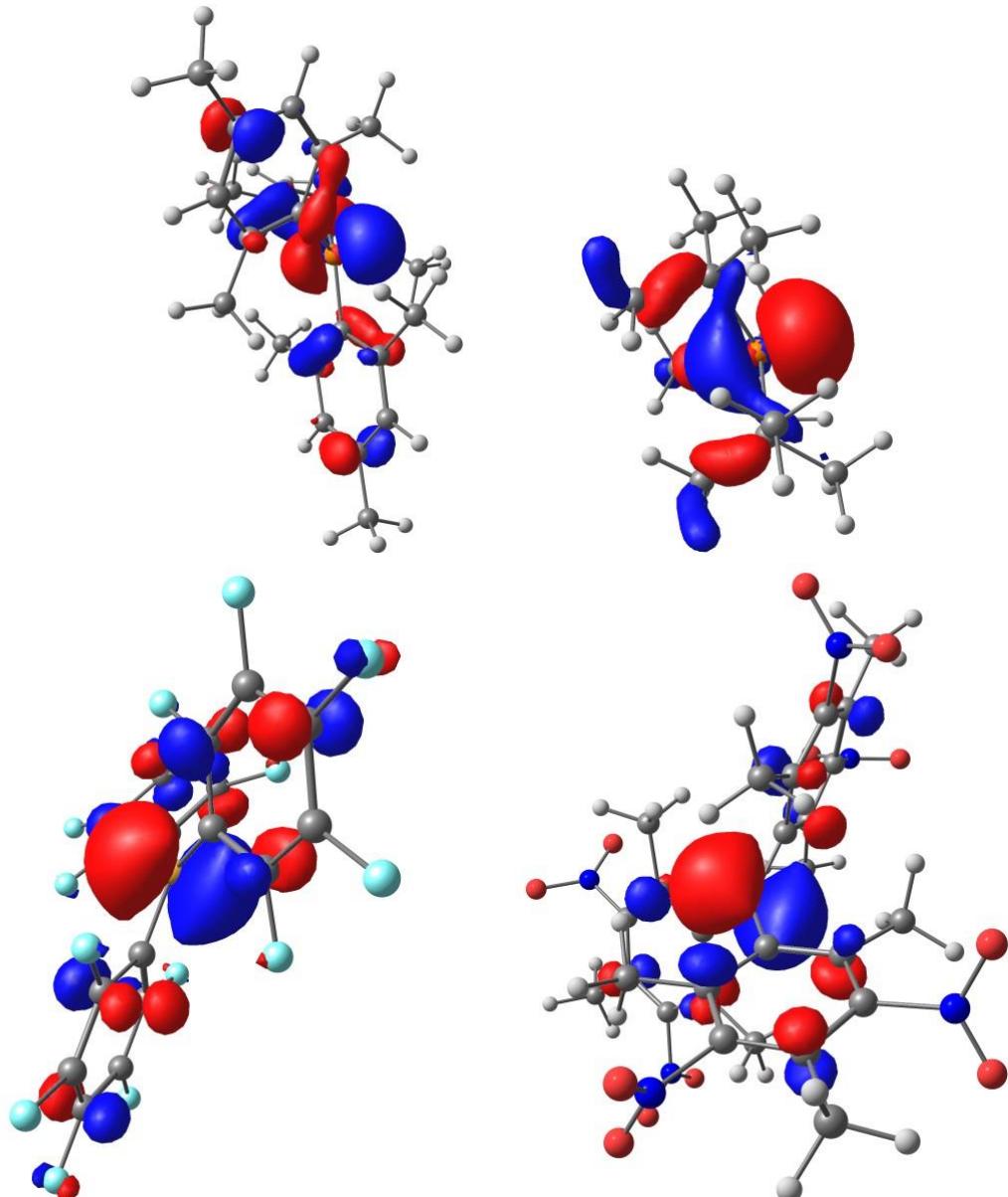
Orbital contribution to CT-band excitation for  $\text{PtBu}_3/\text{B}(\text{C}_6\text{F}_5)_3$ :

# 1 223 -> 224 Coeff.: 0.69565 Contri.: 96.7858%

223 = HOMO, 224 = LUMO

## SUPPORTING INFORMATION

## SOMOs



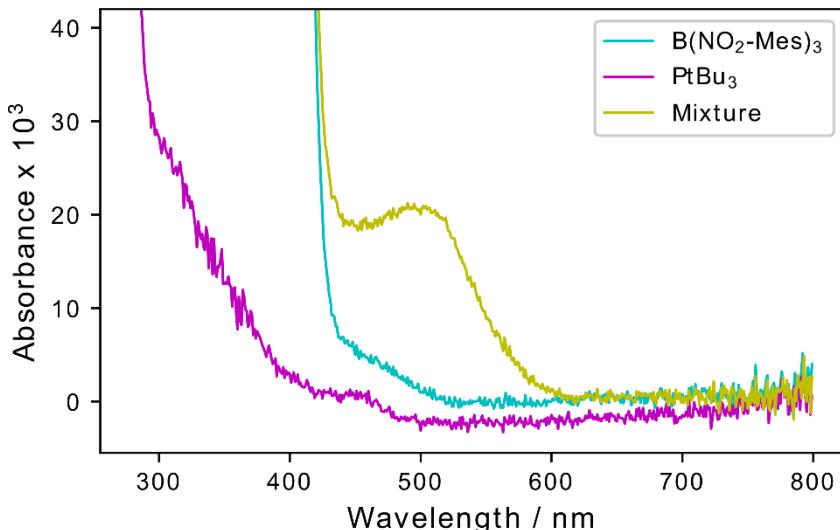
**Figure S13:** SOMOs of the different radicals formed after excitation of the CT-complexes.  $\text{PMes}_3^{\bullet+}$  (top left),  $\text{PtBu}_3^{\bullet+}$  (top right),  $\text{B}(\text{C}_6\text{F}_5)_3^{\bullet-}$  (bottom left),  $\text{B}(\text{NO}_2\text{-Mes})_3^{\bullet-}$  (bottom right).

## SUPPORTING INFORMATION

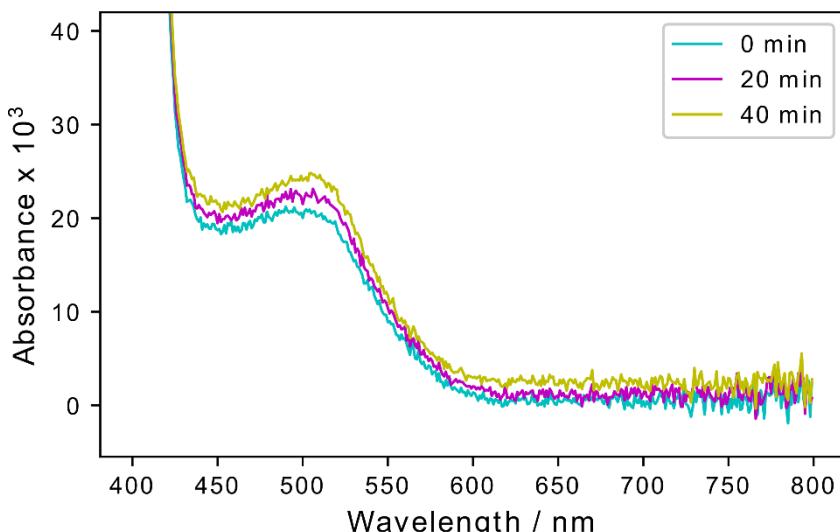
## 4. UV-Vis absorption spectroscopy

**PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub>**

In this case no CT-band is observed. The UV-Vis spectrum features the build-up of the B(NO<sub>2</sub>-Mes)<sub>3</sub><sup>·-</sup> radical anion around 500 nm. This is the result of SET and subsequent degradation of the PtBu<sub>3</sub><sup>+</sup> radical cation which prevents BET. The B(NO<sub>2</sub>-Mes)<sub>3</sub><sup>·-</sup> radical anion grows slowly, as can be seen in Figure S14. Over 24 hours the signal becomes very clear (Figure S15).



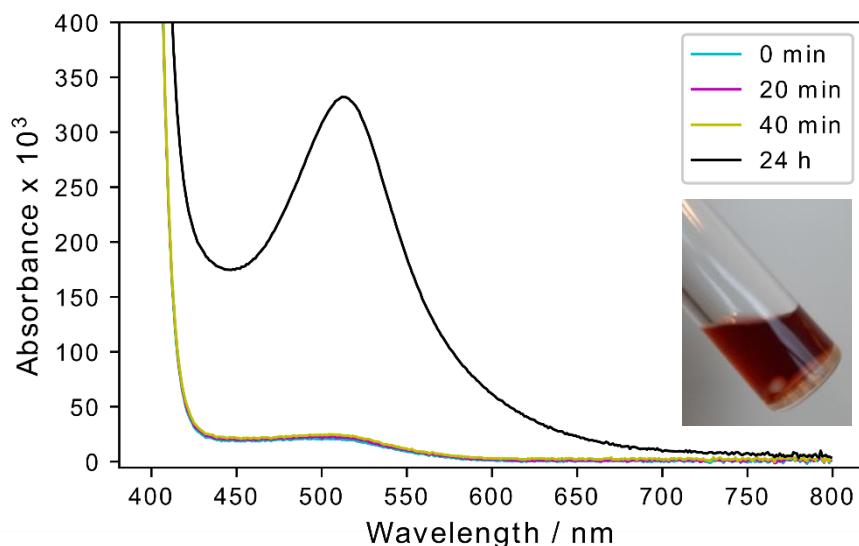
**Figure S14.** UV-Vis spectrum of PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> (both components:  $1.5 \times 10^{-2}$  M in DCM) compared to the separate components ( $1.5 \times 10^{-2}$  M)



**Figure S15.** UV-Vis spectrum of PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> (both components:  $1.5 \times 10^{-2}$  M in DCM) at 3 different time intervals. 0 min is directly after making the sample in the glovebox and transferring it to the spectrometer

SUPPORTING INFORMATION

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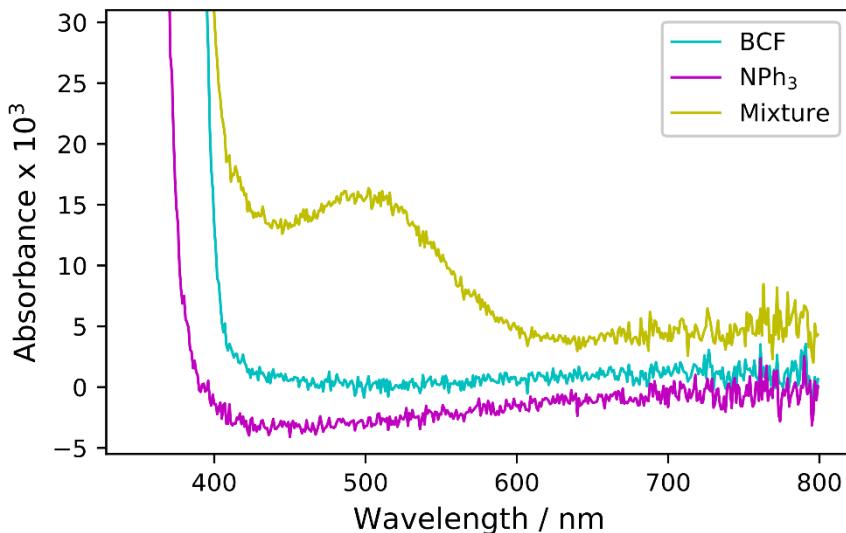


**Figure S16.** UV-Vis spectrum of  $\text{PtBu}_3/\text{B}(\text{NO}_2\text{-Mes})_3$  (both components:  $1.5 \times 10^{-2}$  M in DCM) at 4 different time intervals. 0 min is directly after making the sample in the glovebox and transferring it to the spectrometer. Picture (right) taken after 24 h

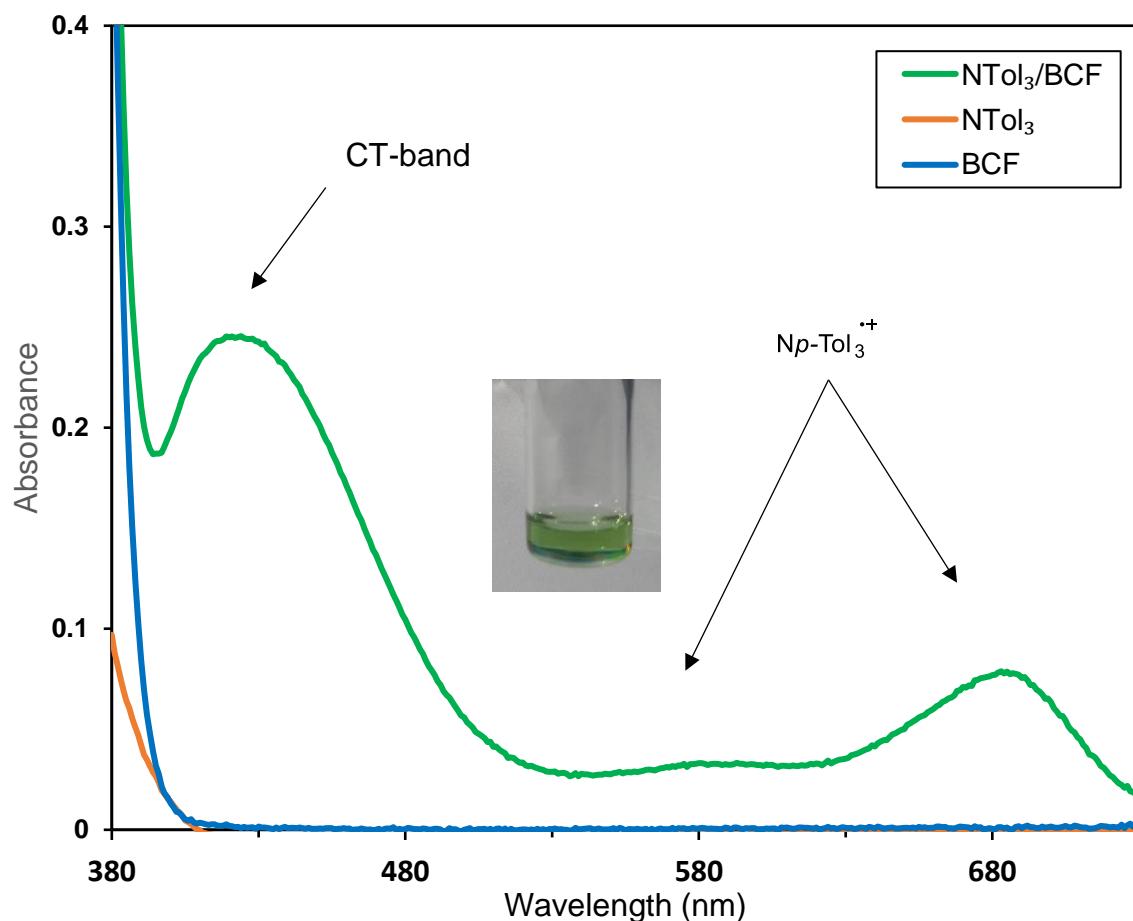
## SUPPORTING INFORMATION

**NPh<sub>3</sub>/BCF and Np-Tol<sub>3</sub>/BCF**

In the case of NPh<sub>3</sub>/BCF, a very weak CT-band is observed. Np-Tol<sub>3</sub> features a much stronger CT-band and bands corresponding amine radical cation ( $\text{Np-Tol}_3^{\cdot+}$ )<sup>7</sup> which builds-up over time as the sample is exposed to more light. This makes the sample turn rapidly from yellow to green (within a few minutes) and then to blue.

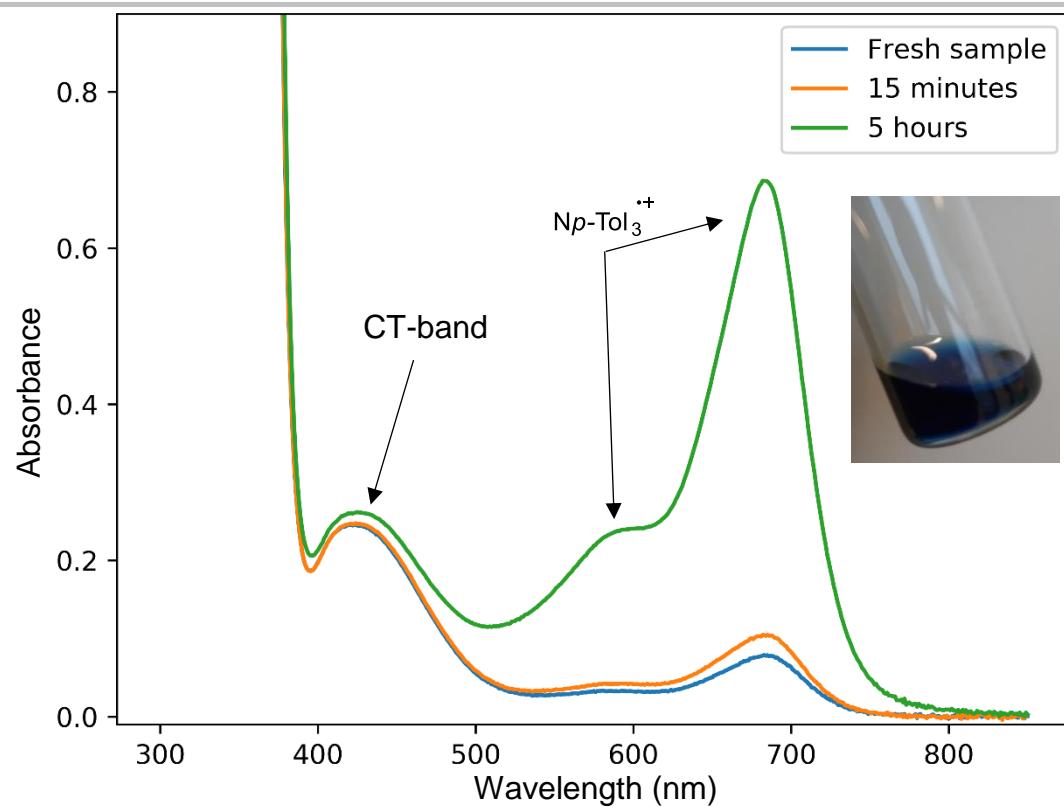


**Figure S17.** UV-Vis spectrum of NPh<sub>3</sub>/BCF (both components:  $1.5 \times 10^{-2}$  M in toluene) compared to the separate components ( $1.5 \times 10^{-2}$  M)



**Figure S18.** UV-Vis spectrum of Np-Tol<sub>3</sub>/BCF (both components:  $1.5 \times 10^{-2}$  M in toluene) compared to the separate components ( $1.5 \times 10^{-2}$  M). Picture shows colour a minute after preparing the sample

## SUPPORTING INFORMATION



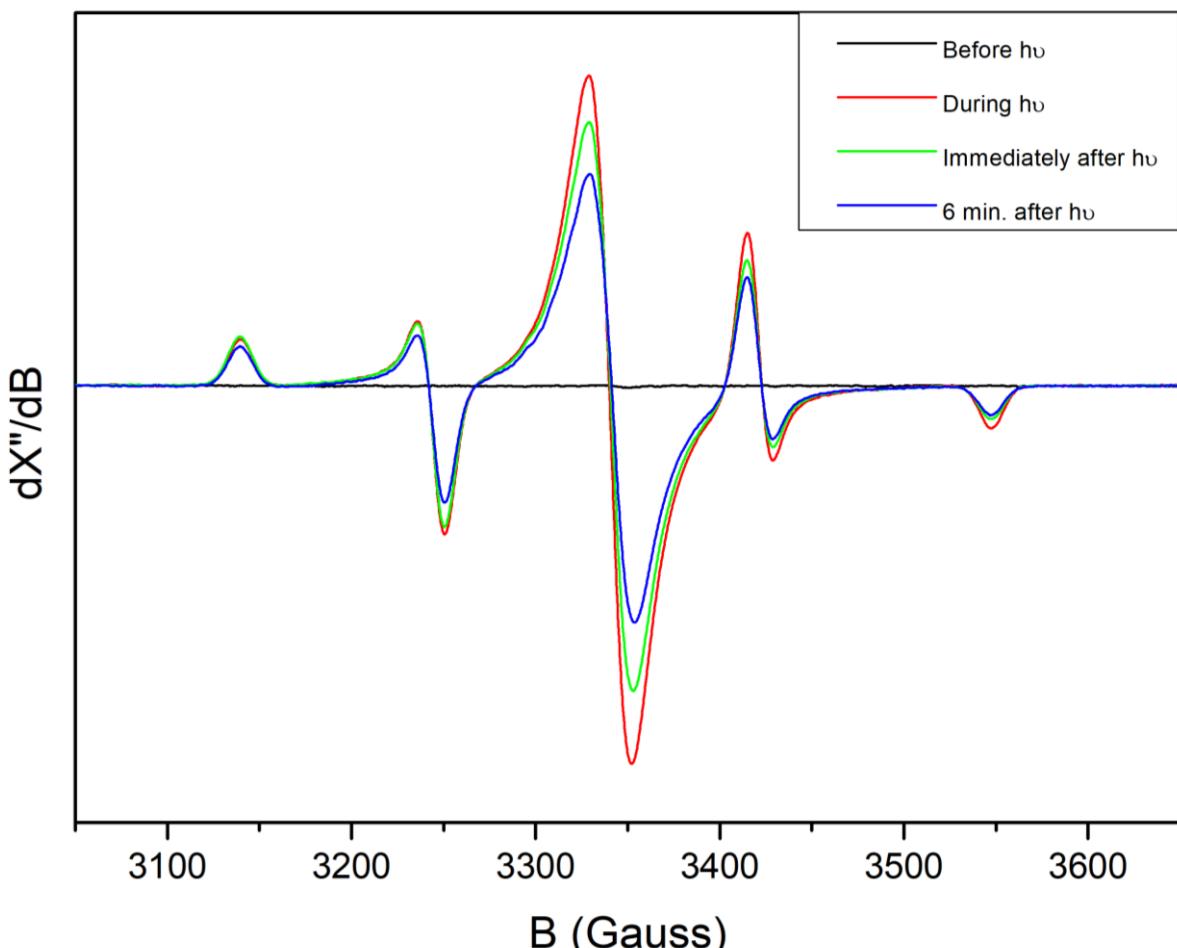
**Figure S19.** UV-Vis spectrum of Np-Tol<sub>3</sub>/BCF (both components:  $1.5 \times 10^{-2}$  M in toluene) immediately after making the sample, 15 minutes later and 5 hours later. Picture (right) shows the colour after several hours

## SUPPORTING INFORMATION

## 5. EPR procedures

**EPR procedure (PMes<sub>3</sub>/BCF and PtBu<sub>3</sub>/BCF) at 30 K**

The phosphine (PMes<sub>3</sub> or PtBu<sub>3</sub>: 0.03 mmol, 1 eq) and borane (BCF: 0.03 mmol, 1 eq) were dissolved together in 0.5 mL toluene. An EPR sample of this solution was frozen using liquid nitrogen before being placed in the EPR spectrometer where it was kept at 30 K during all measurements. The sample was measured before, during, immediately after, and 6 minutes after a 90 second irradiation with visible light (390nm – 500nm). It is worth noting that the colour from the radical dissipates immediately on thawing the solution.

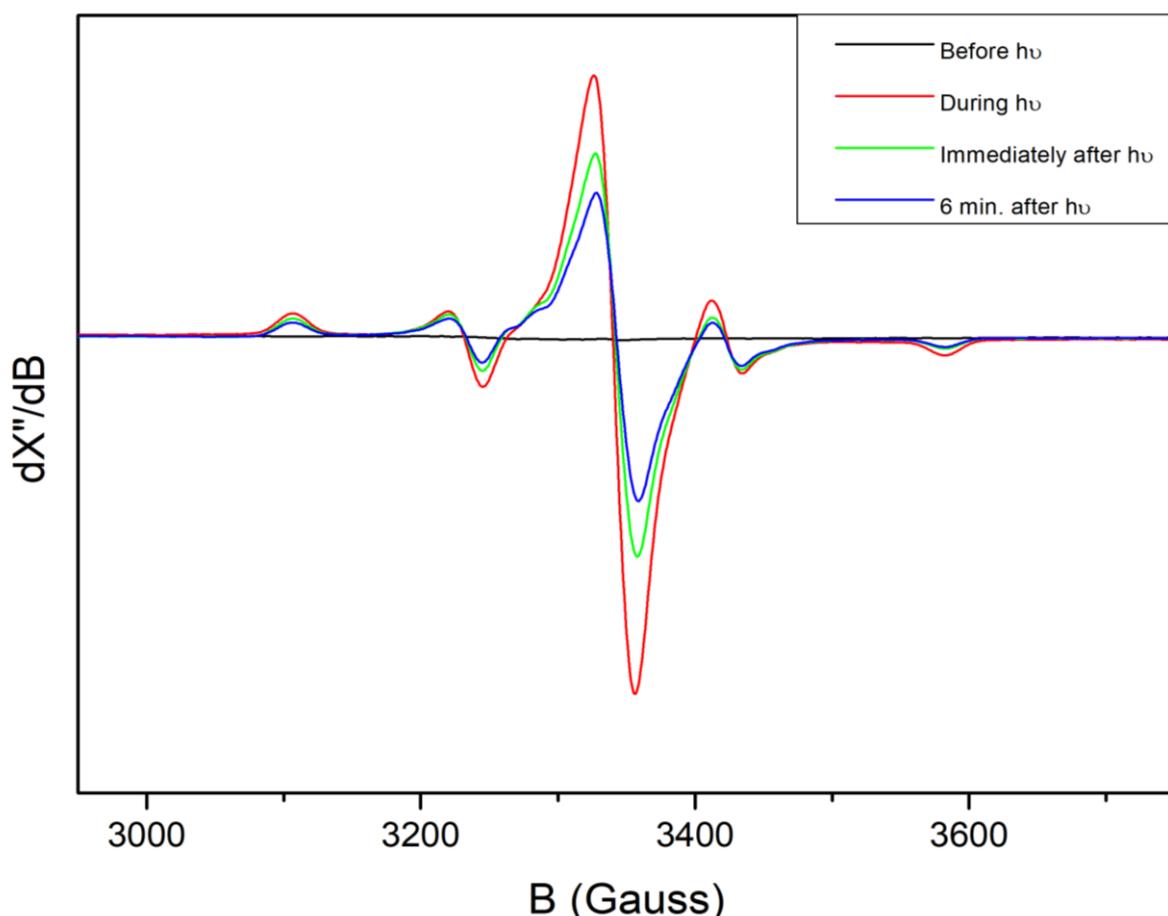


**Figure S20.** EPR spectrum of PMes<sub>3</sub>/BCF in toluene at 30K, measured before, during and after irradiation with visible light (390–500 nm)

**Table S12.** EPR experiment acquisition details for PMes<sub>3</sub>/BCF

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
Before hν	9.375552	2.000	0.6325
During hν	9.375449	2.000	0.6325
After hν	9.375447	2.000	0.6325
6 min after hν	9.375510	2.000	0.6325

## SUPPORTING INFORMATION

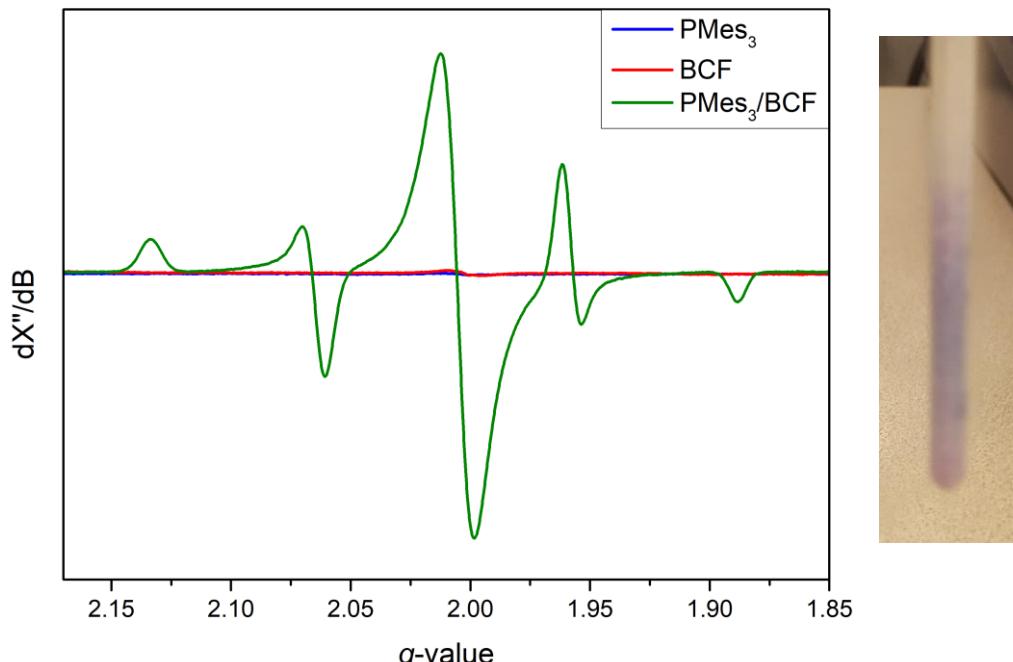


**Figure S21.** EPR spectrum of  $\text{PtBu}_3/\text{BCF}$  in toluene at 30 K, measured before, during and after irradiation with visible light (390 nm – 500 nm)

**Table S13:** EPR experiment acquisition details for  $\text{PtBu}_3/\text{BCF}$

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
Before $h\nu$	9.376670	8.000	6.325
During $h\nu$	9.376565	8.000	6.325
After $h\nu$	9.376594	8.000	6.325
6 min after $h\nu$	9.376624	8.000	6.325

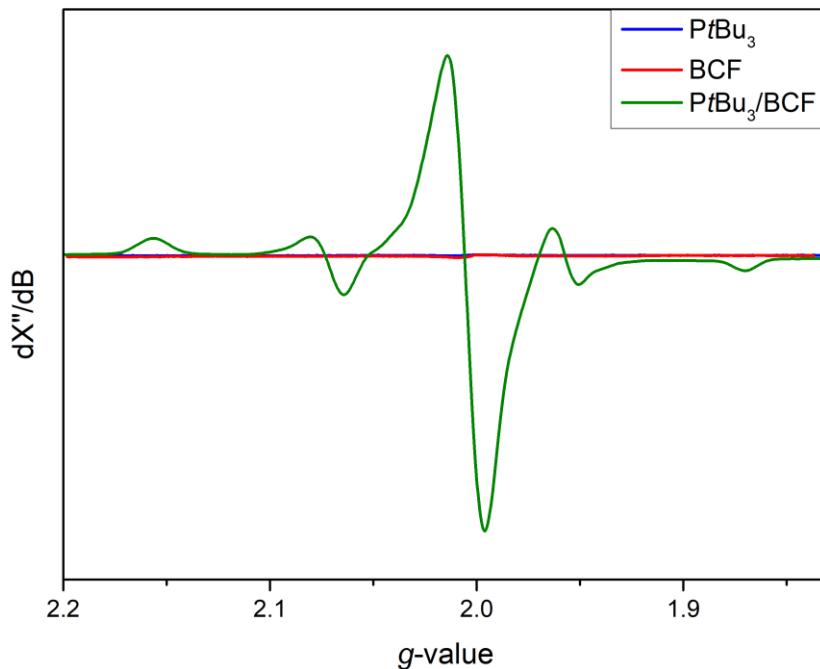
## SUPPORTING INFORMATION

EPR control experiments (PMes<sub>3</sub>/BCF and PtBu<sub>3</sub>/BCF)

**Figure S22.** EPR spectra in toluene at 30 K during irradiation with visible light (390 – 500 nm) for PMes<sub>3</sub> and BCF separately and together. The sample is dark purple when removed from the EPR (right) but reverts back to pink

**Table S14.** EPR experiment acquisition details for the separate phosphines and borane.

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
PMes <sub>3</sub>	9.360534	2.000	6.325
PtBu <sub>3</sub>	9.362350	2.000	6.325
BCF	9.383787	2.000	6.325

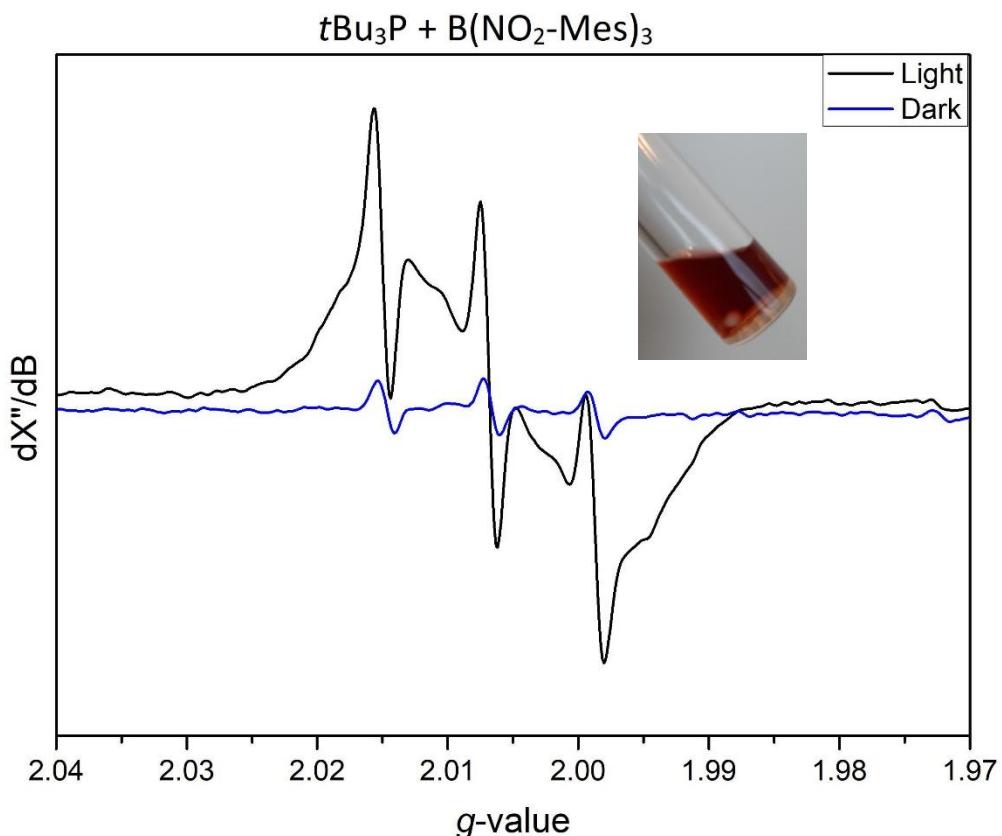


**Figure S23.** EPR spectra in toluene at 30 K during irradiation with visible light (390 – 500 nm) for PtBu<sub>3</sub> and BCF separately and together

## SUPPORTING INFORMATION

**EPR procedure  $t\text{Bu}_3\text{P}/\text{B}(\text{NO}_2\text{-Mes})_3$** 

The phosphine ( $t\text{Bu}_3\text{P}$ : 0.03 mmol, 1 eq) and borane ( $\text{B}(\text{NO}_2\text{-Mes})_3$ : 0.03 mmol, 1 eq) were dissolved together in 0.5 mL dichloromethane to yield a pale yellow solution. Two samples were prepared of which one was kept in the dark while the other was irradiated with 455 nm light (High power LEDS: OSRAM Oslon SSL 80) for 3 hours using the LED-setup described below (Figure S43). The dark sample showed no change whereas the irradiated sample became dark red and  $^{31}\text{P}$ -NMR showed indication of degradation of the  $\text{PtBu}_3^{*+}$  radical cation with a conversion of 70%. EPR spectroscopy showed evidence of the  $\text{B}(\text{NO}_2\text{-Mes})_3^{*-}$  radical anion.

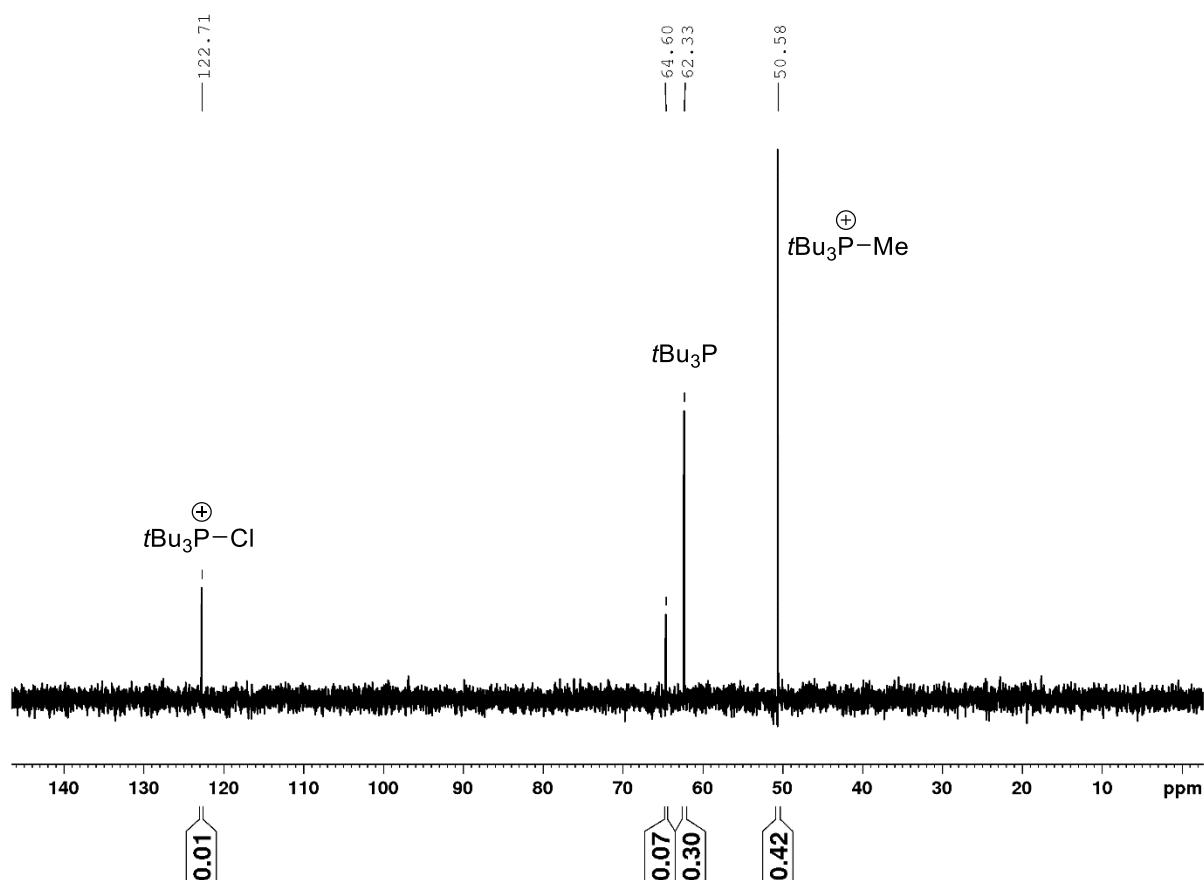


**Figure S24.** EPR spectrum of  $\text{PtBu}_3/\text{B}(\text{NO}_2\text{-Mes})_3$  in DCM at ambient temperature of a sample irradiated (455 nm) for 3h and sample kept in the dark.

**Table S15.** EPR experiment acquisition details for  $\text{PtBu}_3/\text{B}(\text{NO}_2\text{-Mes})_3$

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
Light	9.386084	2.000	6.325
Dark	9.387073	2.000	6.325

## SUPPORTING INFORMATION

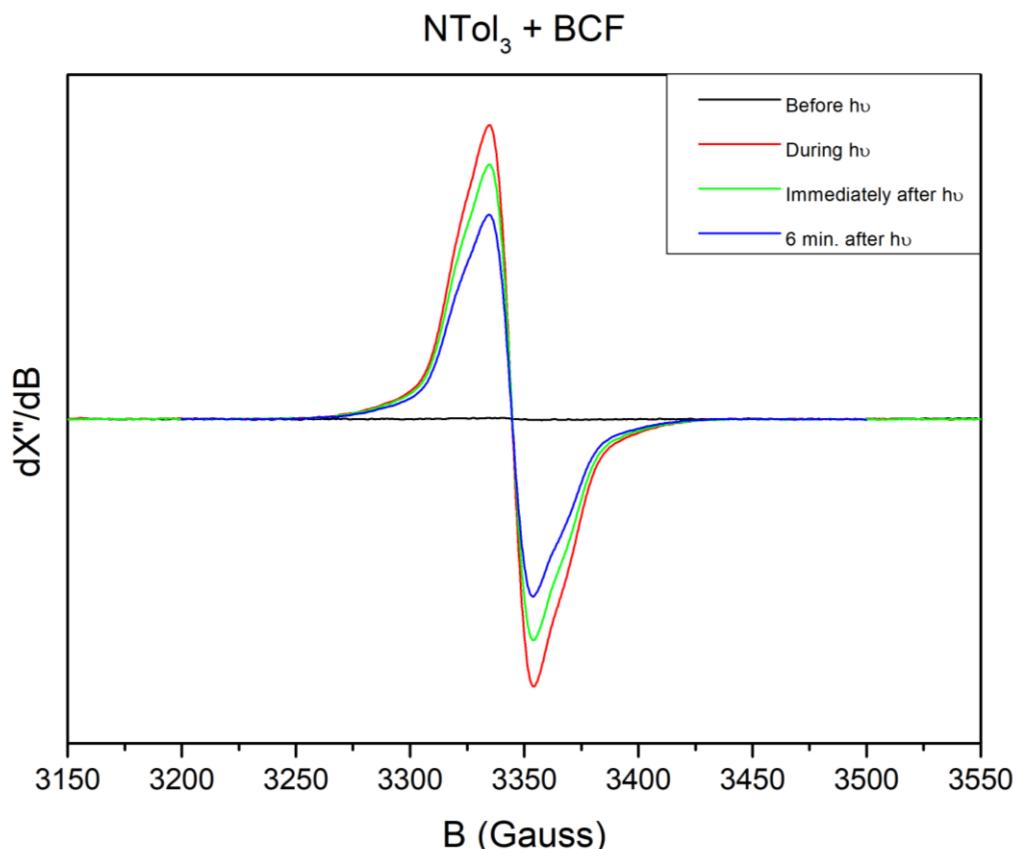


**Figure S25.**  ${}^{31}\text{P}$ -NMR spectrum of  $\text{PtBu}_3/\text{B}(\text{NO}_2\text{-Mes})_3$  in DCM at ambient temperature after 3h irradiation (455 nm)

## SUPPORTING INFORMATION

**EPR procedure ( $\text{NpTol}_3/\text{BCF}$ ) at 80 K**

The amine ( $\text{NpTol}_3$ , 0.03 mmol, 1 eq) and borane (BCF: 0.03 mmol, 1 eq) were dissolved together in 0.5 mL toluene. An EPR sample of this solution was frozen using liquid nitrogen before being placed in the EPR spectrometer where it was kept at 80 K during all measurements. The sample was measured before, during, immediately after, and 6 minutes after a 90 second irradiation with visible light (390nm – 500nm). 80 K was used instead of 30 K to see whether slightly elevating the temperature would lead to visible hyperfine. However, the signal shows no clear hyperfine, which in combination with both radicals ( $\text{NpTol}_3^{+*}$  and  $\text{BCF}^{-*}$ ) having a very similar g-value makes it impossible to determine whether both radicals ( $\text{NpTol}_3^{+*}$  and  $\text{BCF}^{-*}$ ) are being observed.



**Figure S26.** EPR spectrum of  $\text{NPh}_3/\text{BCF}$  in toluene at ambient temperature, measured before, during and after irradiation with visible light (390–500 nm)

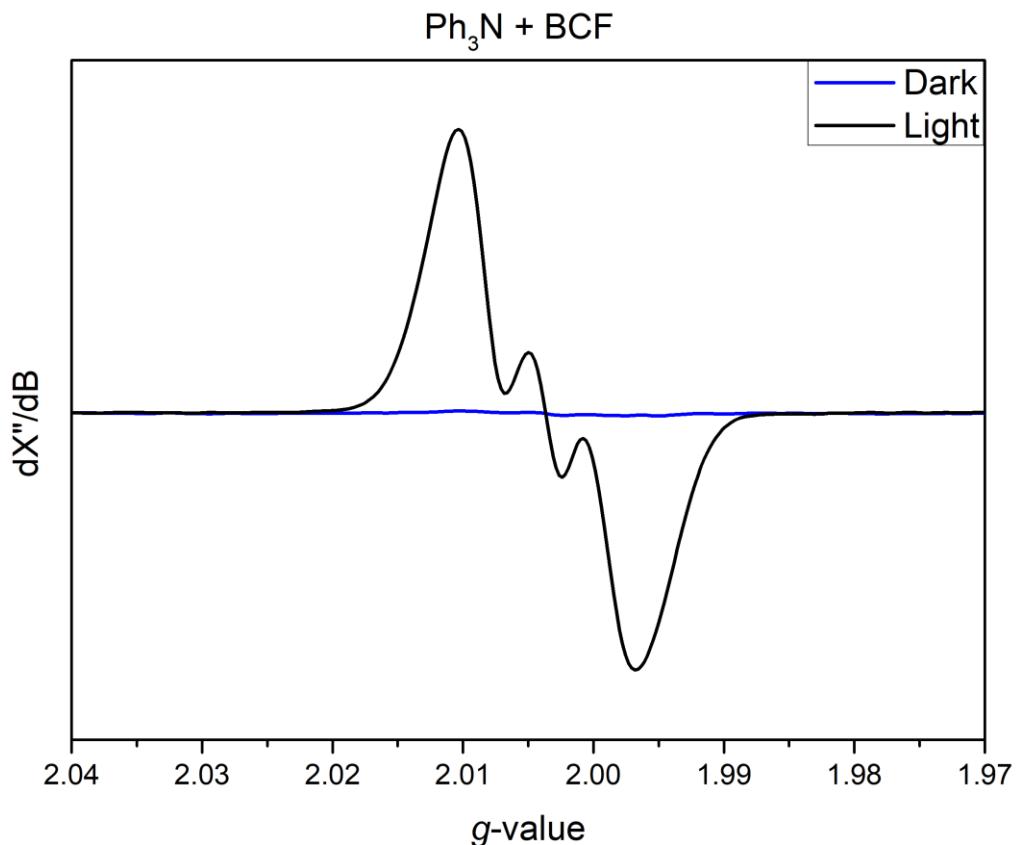
**Table S16.** EPR experiment acquisition details for  $\text{NpTol}_3/\text{BCF}$  at 80K

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
Before $h\nu$	9.376183	2.000	0.07962
During $h\nu$	9.376084	2.000	0.07962
After $h\nu$	9.376105	2.000	0.07962
6 min after $h\nu$	9.375510	2.000	0.07962

## SUPPORTING INFORMATION

**EPR procedure ( $\text{NPh}_3/\text{BCF}$  and  $\text{Np-Tol}_3/\text{BCF}$ ) at rt.**

The amine ( $\text{Ph}_3\text{N}$  or  $p\text{Tol}_3\text{N}$ : 0.03 mmol, 1 eq) and borane (BCF: 0.03 mmol, 1 eq) were dissolved together in 0.5 mL toluene. An EPR sample of this solution was measured at room temperature. The sample was measured before, during, and immediately after a 90 second irradiation with visible light (390nm – 500nm). The spectra during and immediately after irradiation showed the same results.

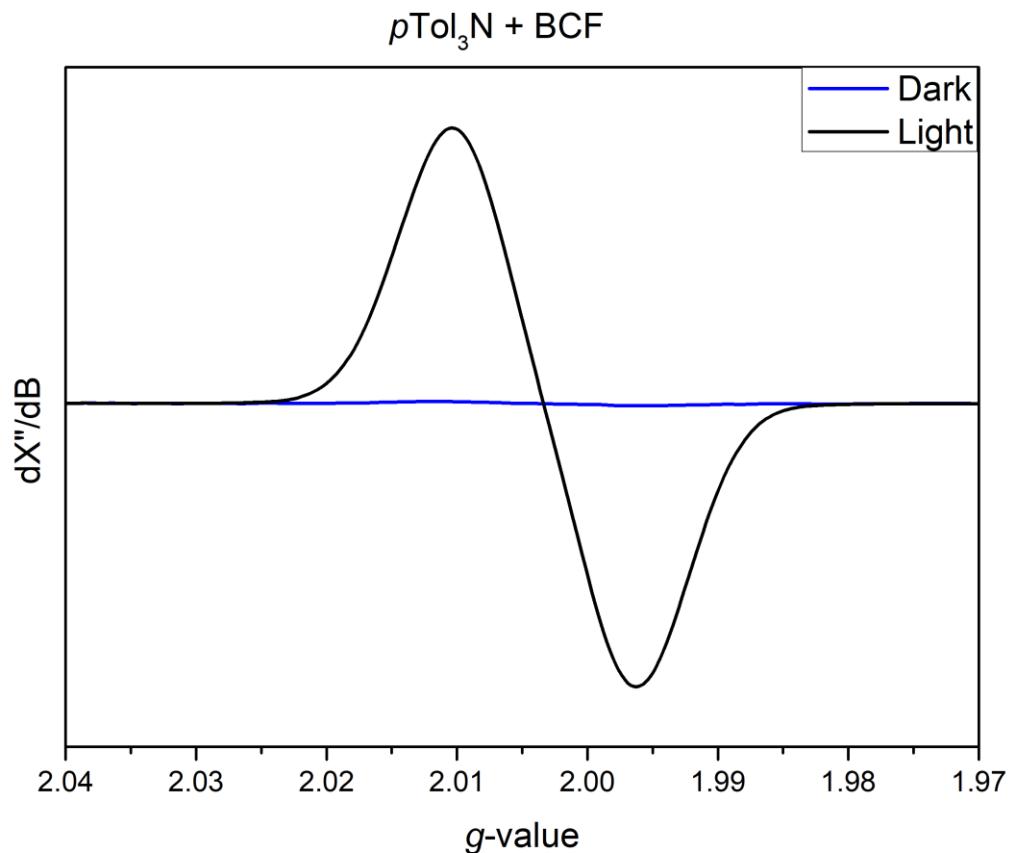


**Figure S27.** EPR spectrum of  $\text{NPh}_3/\text{BCF}$  in toluene at ambient temperature, measured before, during and after irradiation with visible light (390–500 nm)

**Table S17.** EPR experiment acquisition details for  $\text{NPh}_3/\text{BCF}$

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
Before hν	9.652317	4.000	0.6325
During hν	9.652120	2.000	0.6325
After hν	9.652145	2.000	0.6325

## SUPPORTING INFORMATION



**Figure S28.** EPR spectrum of  $\text{NpTol}_3/\text{BCF}$  in toluene at ambient temperature, measured before, during and after irradiation with visible light (390–500 nm)

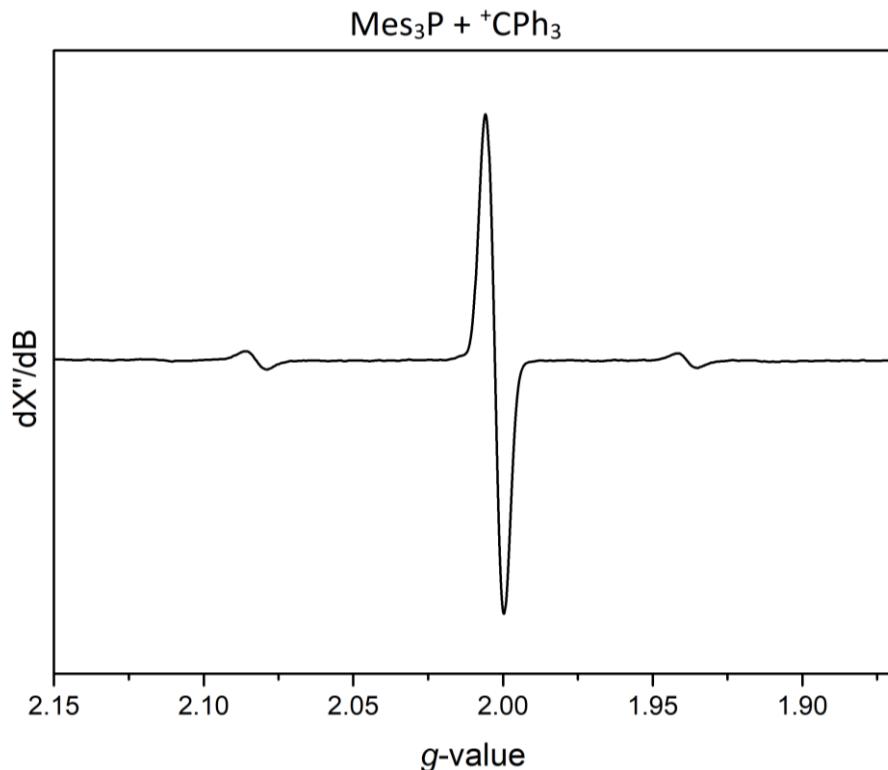
**Table S18.** EPR experiment acquisition details for  $\text{NpTol}_3/\text{BCF}$

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
Before hv	9.651501	4.000	0.6325
During hv	9.651357	4.000	0.6325
After hv	9.651263	4.000	0.6325

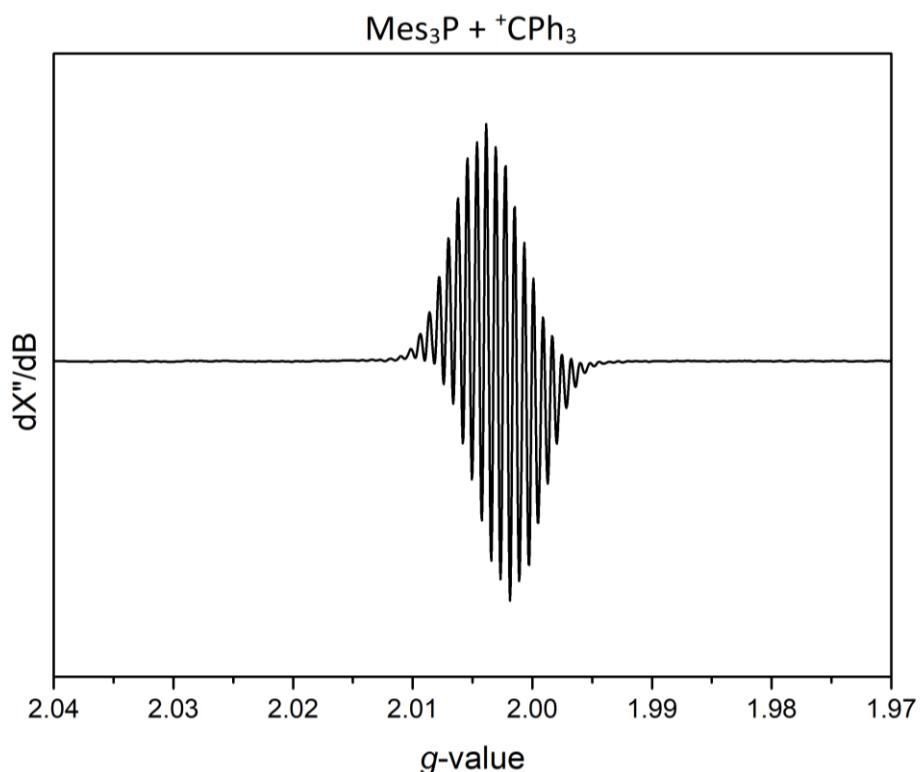
## SUPPORTING INFORMATION

**EPR procedure ( $\text{PMes}_3/\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$ ,  $\text{PtBu}_3/\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$ ,  $\text{NPh}_3/\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$  and  $\text{Np-Tol}_3/\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$ ) at rt.**

The phosphine or amine ( $\text{PMes}_3$ ,  $\text{PtBu}_3$ ,  $\text{NPh}_3$  or  $\text{Np-Tol}_3$ : 0.03 mmol, 1 eq) and trityl source ( $\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$ : 0.03 mmol, 1 eq) were dissolved together in 0.5 mL toluene. An EPR sample of this solution measured at room temperature. Samples prepared in the light and the dark showed the exact same results.

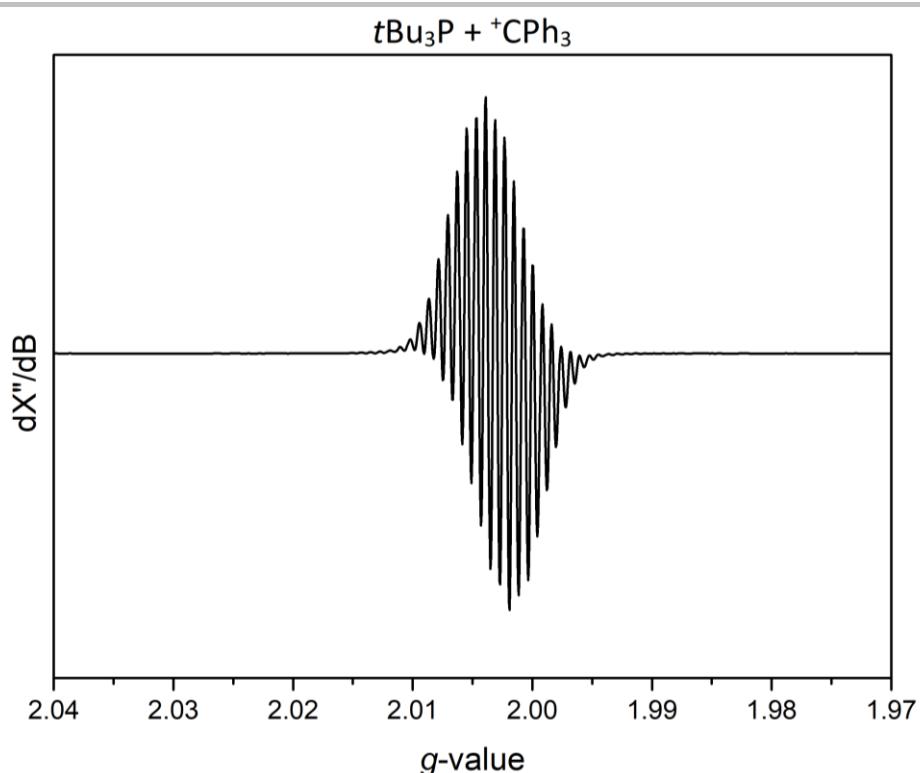


**Figure S29.** EPR spectrum of  $\text{PMes}_3/\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$  in toluene at ambient temperature

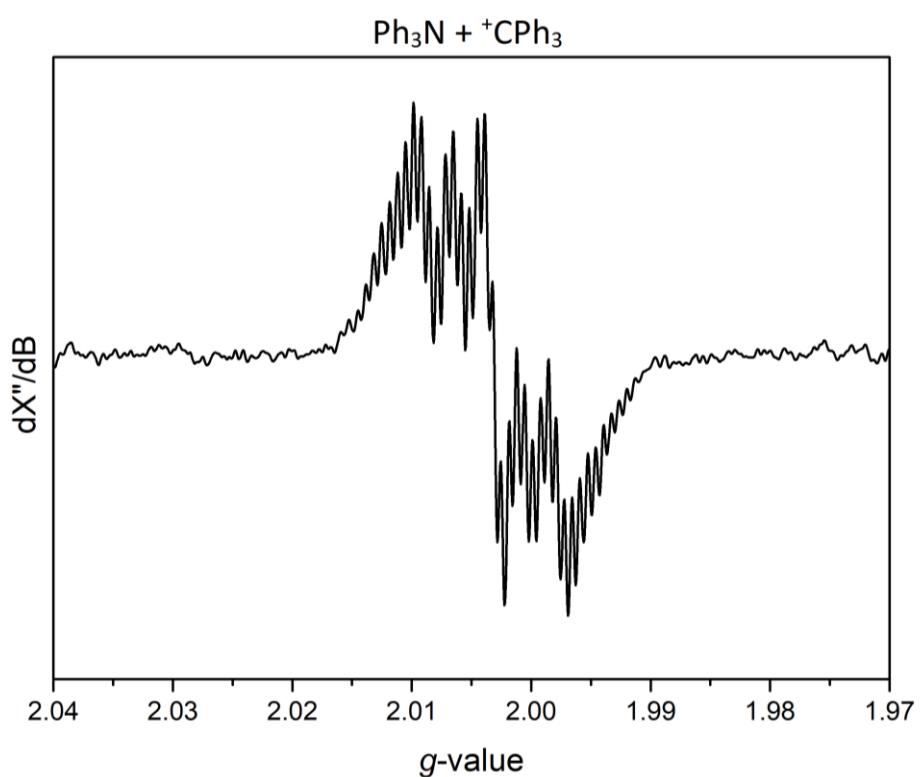


**Figure S30.** EPR spectrum of  $\text{PMes}_3/\text{[Ph}_3\text{C][B(C}_6\text{F}_5)_4]$  in toluene at ambient temperature zoomed in

## SUPPORTING INFORMATION

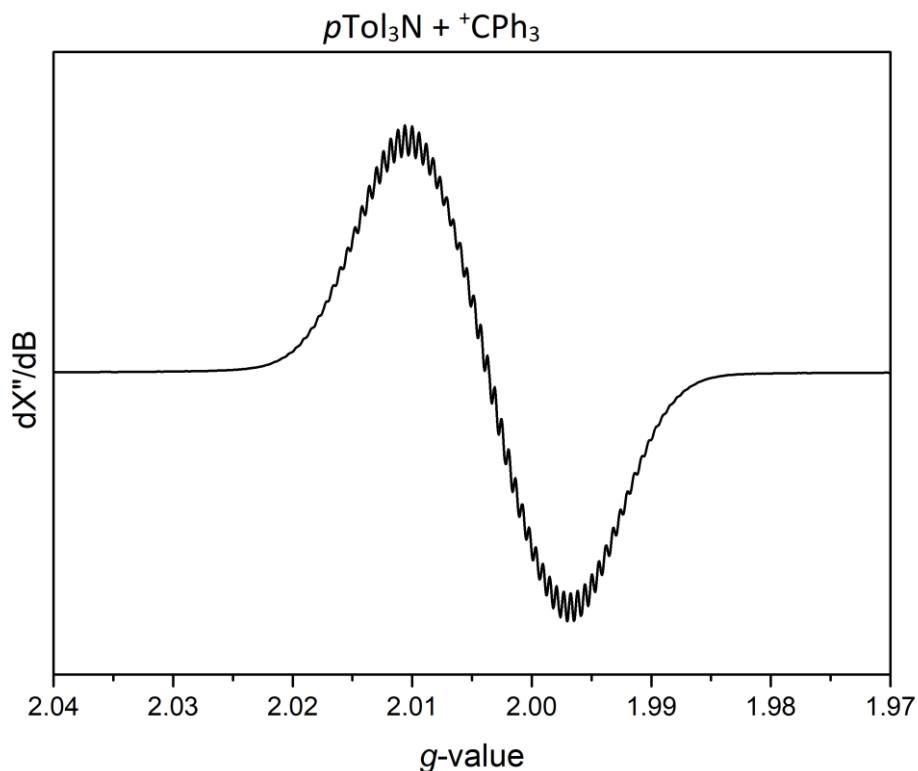


**Figure S31.** EPR spectrum of  $\text{PtBu}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene at ambient temperature



**Figure S32.** EPR spectrum of  $\text{NPh}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene at ambient temperature

## SUPPORTING INFORMATION



**Figure S33** EPR spectrum of *p*Tol<sub>3</sub>N/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene at ambient temperature

**Table S19.** EPR experiment acquisition details for phosphine or amine/<sup>3</sup>CPh<sub>3</sub> combinations

	Microwave frequency (GHz)	Modulation amplitude (G)	Power (mW)
PMes <sub>3</sub> / <sup>3</sup> CPh <sub>3</sub>	9.381985	4.000	0.6325
PMes <sub>3</sub> / <sup>3</sup> CPh <sub>3</sub> Zoom	9.381995	1.000	0.6325
PtBu <sub>3</sub> / <sup>3</sup> CPh <sub>3</sub>	9.381213	1.000	0.6325
NPh <sub>3</sub> / <sup>3</sup> CPh <sub>3</sub>	9.383135	1.000	0.6325
Np-Tol <sub>3</sub> / <sup>3</sup> CPh <sub>3</sub>	9.380745	1.000	0.6325

**SUPPORTING INFORMATION****Calculations EPR concentrations:**

Boltzmann distribution:  $F_2/F_1 = e^{\Delta E/kT}$  (For which  $F_2/F_1$  is the population ratio between the two energy levels)

For PMes<sub>3</sub><sup>+</sup>/CPh<sub>3</sub>:

$$\Delta E = 7.0 \text{ kcal/mol}$$

$$1 \text{ kcal/mol} = 4.184 \text{ kJ/mol} = 6.9477 \times 10^{-21} \text{ J / molecule}$$

$$\Delta E = 4.86339 \times 10^{-20} \text{ J}$$

$$F_2/F_1 = 7.35153 \times 10^{-6} / 1$$

$$\text{So ratio PMes}_3^+/\text{CPh}_3 : \text{PMes}_3^{++}/\text{CPh}_3 = 1 : 7.35153 \times 10^{-6}$$

For the EPR measurement, the starting concentration was 0.03 M

$$\text{Concentration of radicals} = 0.06 / (1 + 7.35153 \times 10^{-6}) * 7.35153 \times 10^{-6} = 4.411 \times 10^{-7} \text{ M}$$

As EPR spectrometers can measure concentrations down to 10<sup>-8</sup> M this thus gives measurable concentrations of both radicals.<sup>8</sup>

**Calculations Gomberg dimerisation concentrations:**

For Dimer/·CPh<sub>3</sub>:

$$\Delta E = 4.8 \text{ kcal/mol}$$

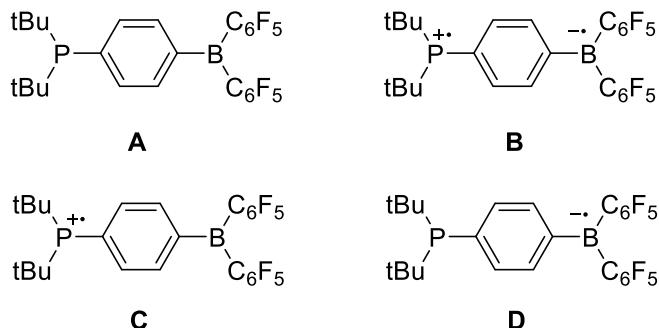
$$1 \text{ kcal/mol} = 4.184 \text{ kJ/mol} = 6.9477 \times 10^{-21} \text{ J / molecule}$$

$$\Delta E = 3.265419 \times 10^{-20} \text{ J}$$

$$F_2/F_1 = 3.57 \times 10^{-4} / 1$$

$$\text{So ratio Dimer}/\cdot\text{CPh}_3 = 1 : 3.5 \times 10^{-4}$$

## SUPPORTING INFORMATION

EPR analysis of possible *para*-addition ( $\text{PtBu}_3 + \text{B}(\text{C}_6\text{F}_5)_3$ ) radicals:**Figure S34.** *Para*-addition product of  $\text{PtBu}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  and possible radical derivatives.

As  $\text{PtBu}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  are known to slowly react to form *para*-addition product **A**, we analysed the possibility of light inducing radical formation starting from species **A** and comparing this with the EPR spectra we obtained (Figure S34).

We measured directly after mixing the Lewis acid and Lewis base to avoid, or at least minimize the formation of compound **A**. We have confirmed this by NMR spectroscopy as we could not detect **A** directly after mixing  $\text{tBu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ . We realize that it is reported<sup>9</sup> that over time  $\text{tBu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  react to form species **A** which exhibits an absorption band at 372 nm. However, the combination of our UV-Vis data with our EPR data leads us to the conclusion that we are observing SET between  $\text{tBu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  rather than excitation of species **A**. Excitation of **A** would lead to generation of biradical **B** for which the EPR signal would feature a much smaller coupling to  $^{31}\text{P}$  than observed in the EPR spectrum (See Table S20). A radical generated from species **A** that would be reasonably be able to match the EPR is data is P-centered radical **C**. However, the two ways this could be generated are both unlikely to occur.

Firstly, species **A** would itself have to form a CT-complex (with either another equivalent of **A** or  $\text{B}(\text{C}_6\text{F}_5)_3$ , which would then be excited to form **C**. As species **A** is present in only minute concentrations directly after addition of  $\text{PtBu}_3$  to  $\text{B}(\text{C}_6\text{F}_5)_3$  (when these measurements were taken) the probability of enough of **A** forming CT-complexes for the resulting radicals to be visible by EPR is very low. Secondly, **C** could be generated by SET from  $\text{PtBu}_3$  to  $\text{B}(\text{C}_6\text{F}_5)_3$  to generate  $\text{PtBu}_3^{+*}$ , and subsequent through solvent tunneling to generate radical **C** and regenerate  $\text{PtBu}_3$ . However, this is also unlikely as the ionization potential of **A** is much higher than that of  $\text{PtBu}_3$  (6.53 eV vs 5.95 eV respectively; wb97xD/6-311+G(d,p); solvent = toluene) making such an electron transfer energetically disfavoured and thus unlikely. In addition, for radical **C** we would expect coupling to a  $^{19}\text{F}$  nucleus, which we do not observe by EPR. These findings lead us to conclude that although we cannot exclude **A** being formed over time and thus added to the absorption band observed by UV-Vis, we can still conclude that a CT-band analogous to the one found for  $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ , must be present by analysing the EPR of the radicals generated by visible light irradiation.

**Table S20.** EPR experiment acquisition details for phosphine or amine/+CPh<sub>3</sub> combinations

Species	$A^{31}\text{P}_1$ (MHz)	$A^{31}\text{P}_2$ (MHz)	$A^{31}\text{P}_3$ (MHz)	Other coupling
Observed: $\text{tBu}_3\text{P}^{+*}$	1365	580	580	
Lit <sup>10</sup> : $\text{tBu}_3\text{P}^{+*}$	1205	851	851	Measured neat, not in a solvent
<i>Computed spectral data</i>				
$\text{tBu}_3\text{P}^{+*}$	1266	375	375	$3 \times ^1\text{H}$ (27-32 MHz)
<b>B</b>	661	234	221	Small coupling to $^1\text{H}$ , $^{10/11}\text{B}$ , $^{19}\text{F}$
<b>C</b>	1354	445	447	$2 \times ^1\text{H}$ (24-41 MHz) and $2 \times ^{19}\text{F}$ (5-74 MHz)

## SUPPORTING INFORMATION

### 6. Transient absorption spectroscopy

The femtosecond transient absorption experiments were performed with a Spectra-Physics Hurricane Ti:sapphire regenerative amplifier system with a repetition rate of 1 kHz, a pulse width of < 200 fs fwhm, and a wavelength of 800 nm. An optical parametric amplifier (OPA 800CF) was used to generate visible pump pulses either by sum-frequency mixing the idler and the 800 nm pump (for making 530 nm) or via frequency-doubling (for making 400 nm). The probe white light with a spectrum spanning 450 nm to 750 nm was produced via supercontinuum generation by attenuating and then focusing 4% of the fundamental into a sapphire plate. A Berek Polarizer (New Focus) was included in the setup in order to provide the magic-angle conditions of the polarization of the pump and probe pulses. The probe light was passed twice through a delay line (Physik Instrumente, M-531DD) that provides an experimental time window of 3.6 ns. The samples were prepared in a glove-box under oxygen-free conditions and placed in quartz cuvettes with 2 mm path lengths (Hellma). After passing through the probe light, the remaining probe light was dispersed by a 150 mm spectrograph (Princeton Instrument SP2150 with a 300 lines per mm grating) and detected with a single-diode array detector (Hamamatsu NMOS S3901-512Q). The readout was done using fast electronics (TEC5). A chopper synchronized to run at ¼ the frequency of the pump (~250 Hz) was used to block every third and fourth pump pulse. The difference absorption spectra were obtained by subtracting the un-pumped absorption spectra from the pumped absorption spectra. The transient data matrices were fitted to sequential kinetic model in python using the least squares method from the SciPy library.<sup>11</sup>

### Sample Preparations

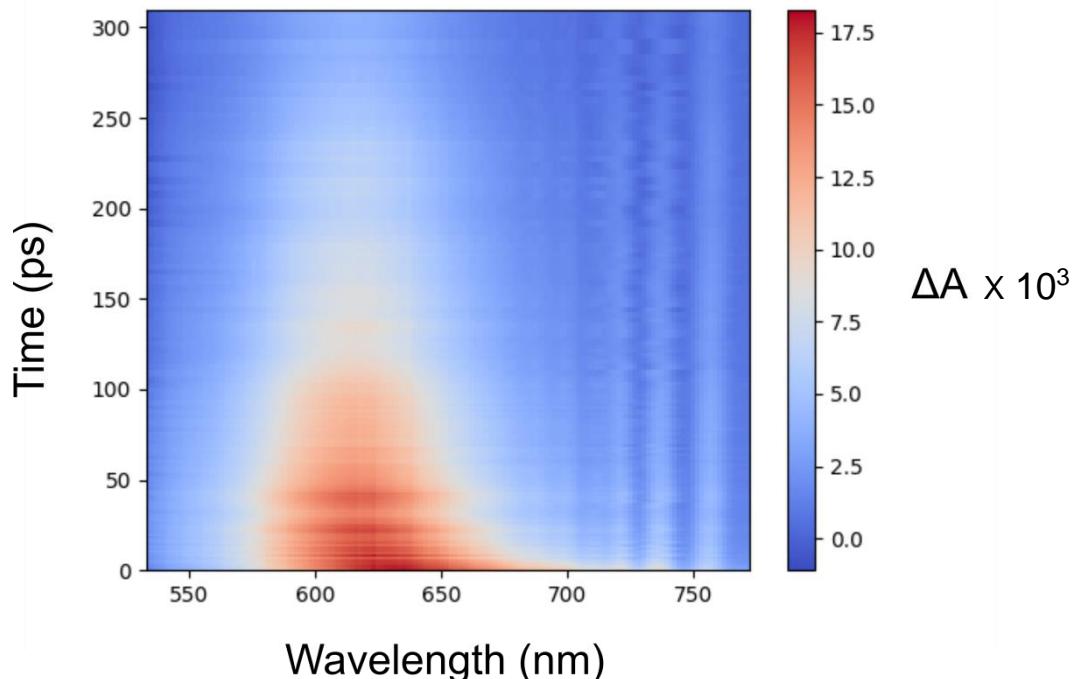
#### PMes<sub>3</sub>/BCF (530 nm)

A 0.04 M (of each component) solution of trimesitylphosphine and BCF in toluene was prepared.

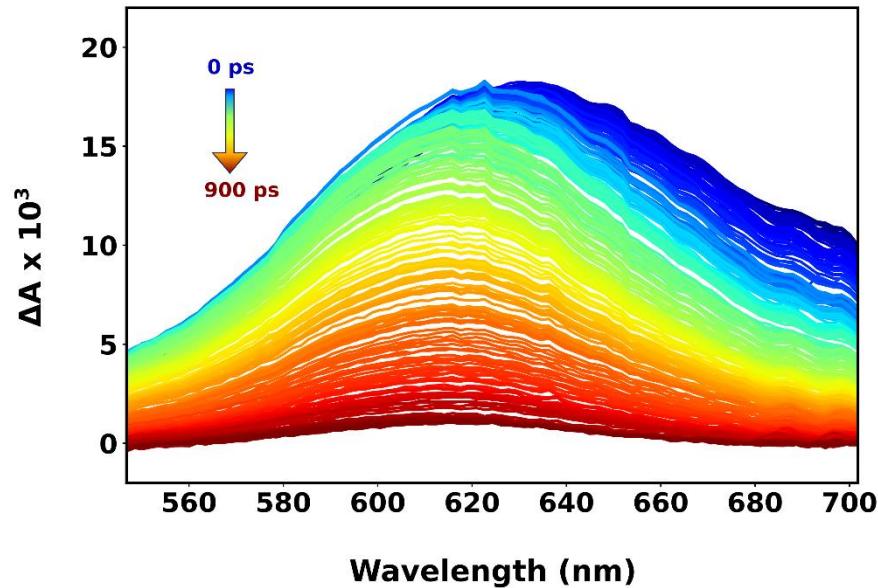
#### PtBu<sub>3</sub>/BCF (400 nm)

A 0.2 M (of each component) solution of tri-*tert*-butylphosphine and BCF in toluene was prepared.

## SUPPORTING INFORMATION

**PMes<sub>3</sub> / BCF**

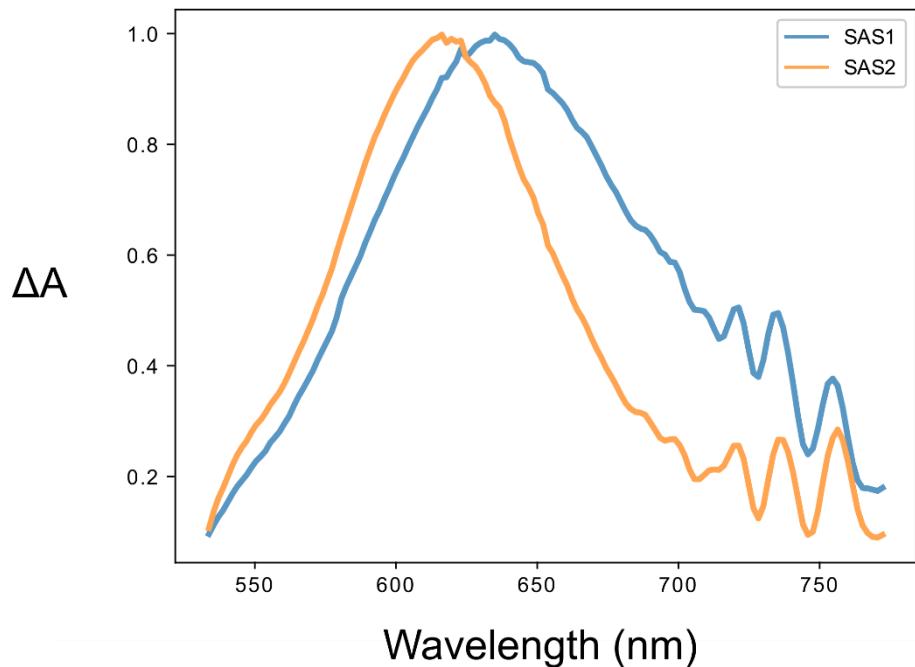
**Figure S35.** Raw transient matrix for transient absorption measurements of the 0.04 M solution of PMes<sub>3</sub>/BCF in toluene



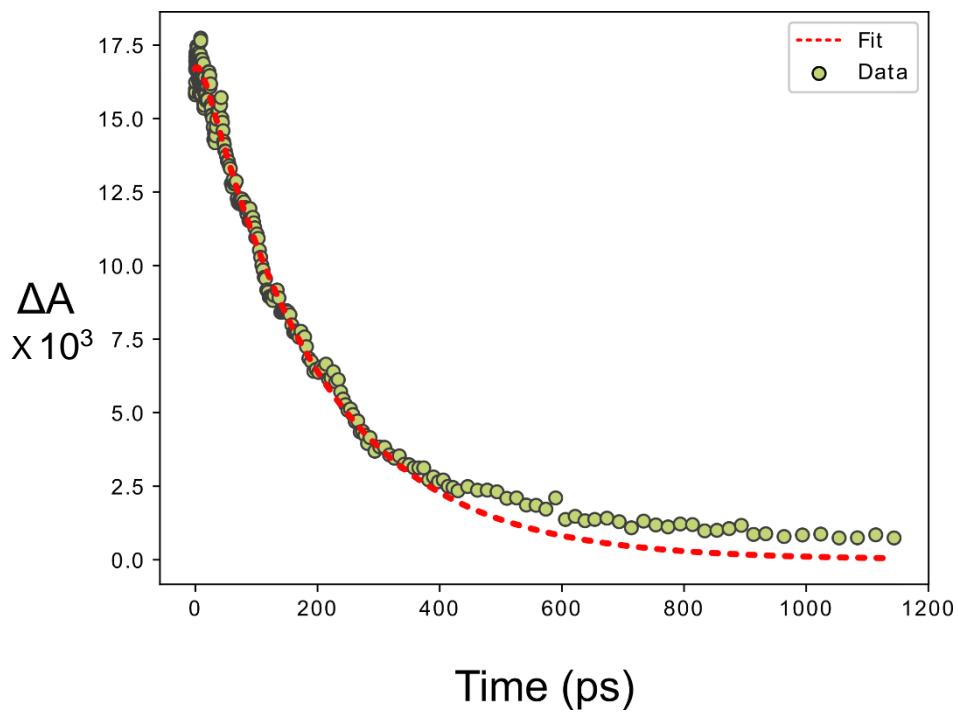
**Figure S36.** Linear Transient Plot for 0.04 M solution of PMes<sub>3</sub>/BCF in toluene after excitation at 530 nm. This is the same figure as shown in the main manuscript. (Figure 3c)

SUPPORTING INFORMATION

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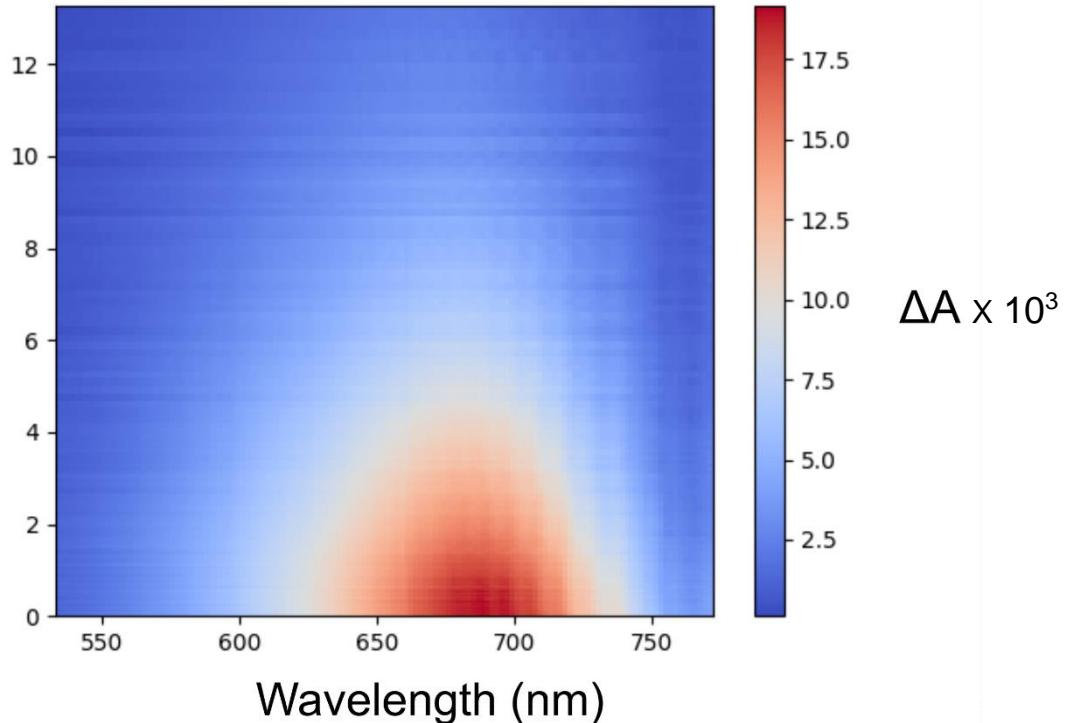


**Figure S37:** Normalized data from figure S35 fitted to a sequential model with two species.  $\tau_1 = 10.19 \pm 0.24$  ps,  $\tau_2 = 194.17 \pm 0.05$  ps

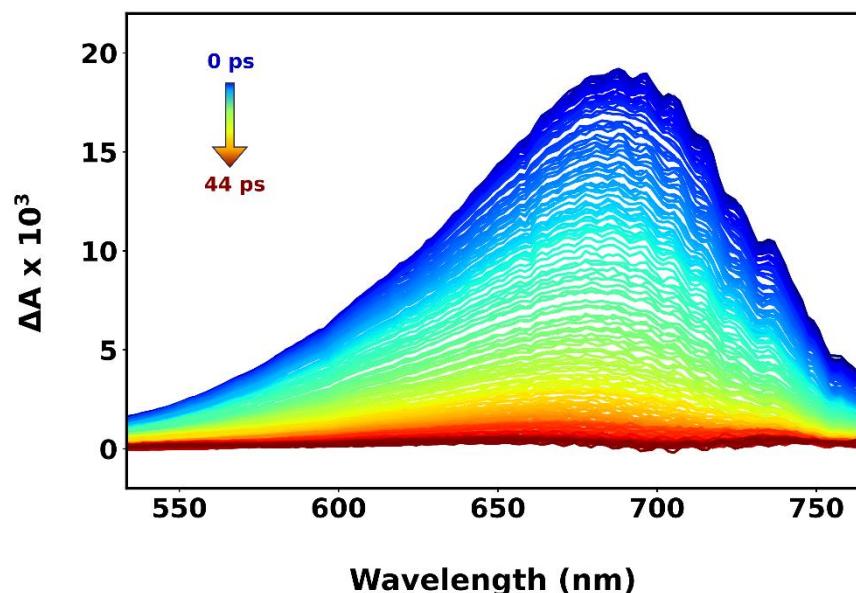


**Figure S38.** Fitted curve of data from Figure S35 at 617 nm

## SUPPORTING INFORMATION

**PtBu<sub>3</sub> / BCF**

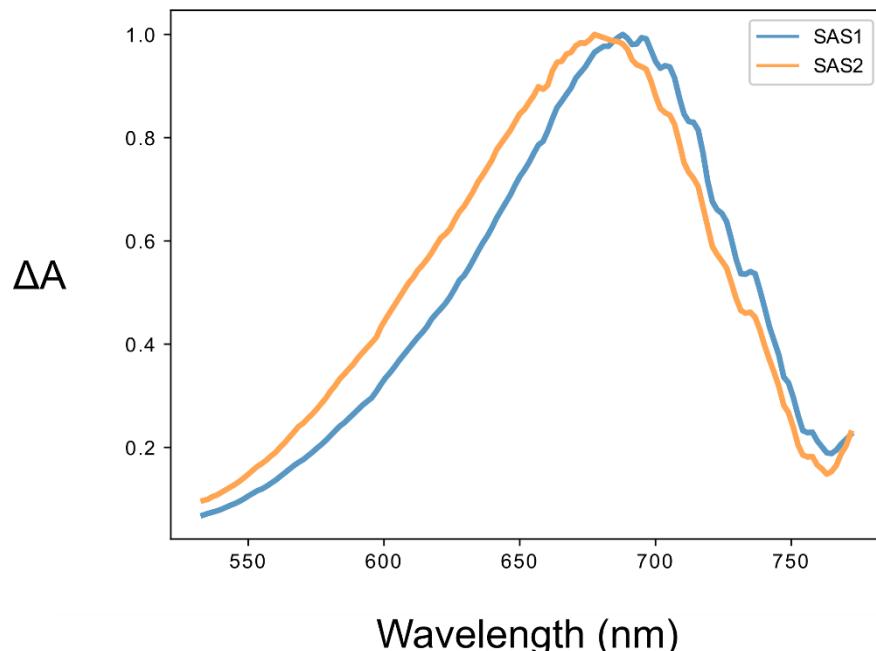
**Figure S39.** Raw transient matrix for measurements of 0.2 M solution of PtBu<sub>3</sub>/BCF in toluene



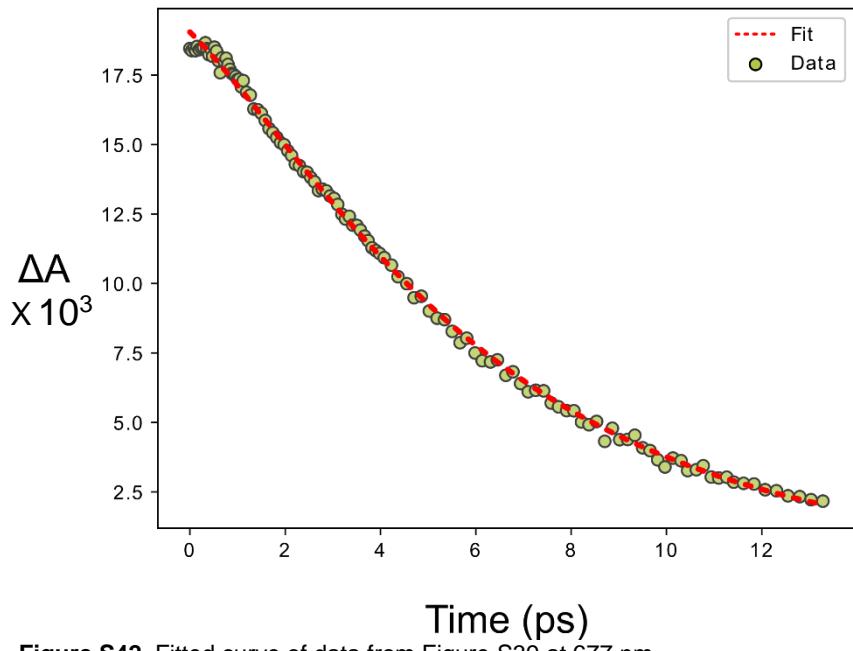
**Figure S40.** Linear transient data for 0.2 M solution of PtBu<sub>3</sub>/BCF in toluene after excitation at 400 nm. This is the same figure as shown in the main manuscript. (Figure 4: right)

SUPPORTING INFORMATION

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**Figure S41.** Normalized data from figure S39 fitted to a sequential model with two species.  $\tau_1 = 1.93 \pm 0.24$  ps,  $\tau_2 = 5.33 \pm 0.02$  ps

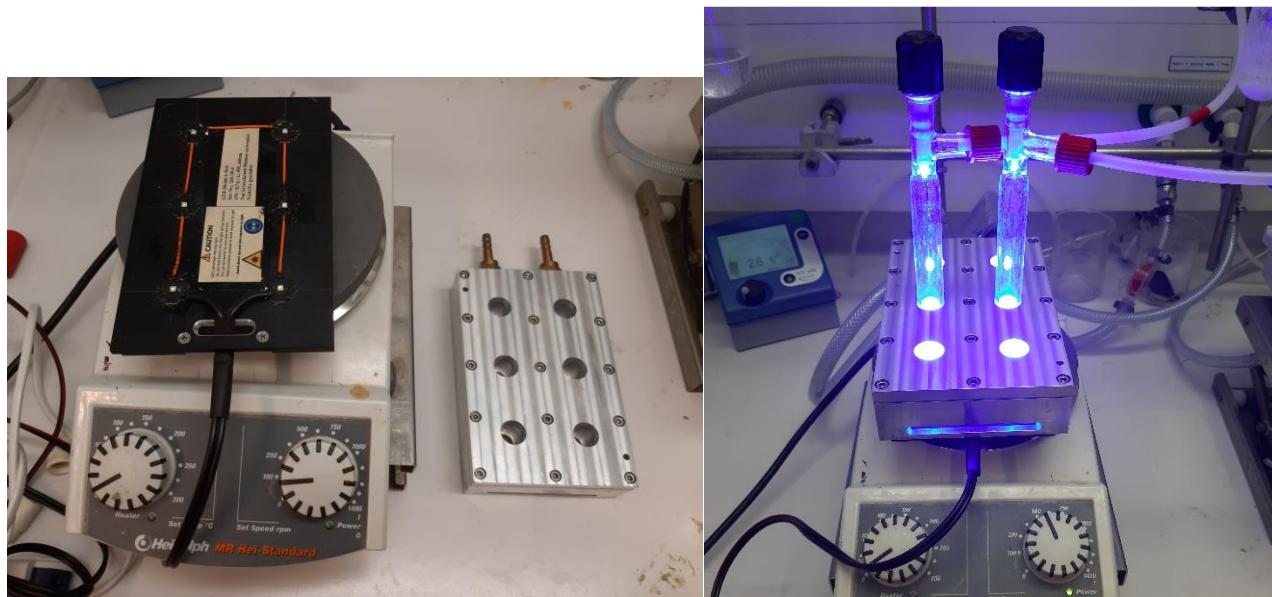


**Figure S42.** Fitted curve of data from Figure S39 at 677 nm

## SUPPORTING INFORMATION

### LED- setup

The LED setup used to irradiate the sample consisted of a LED plate and water-cooled block which keeps the samples at near ambient temperature. The cooling block is mounted on the LED plate after which flat bottomed Schlenks are placed into the holes of the cooling plate. These Schlenks are made to fit exactly so that cooling functions properly.



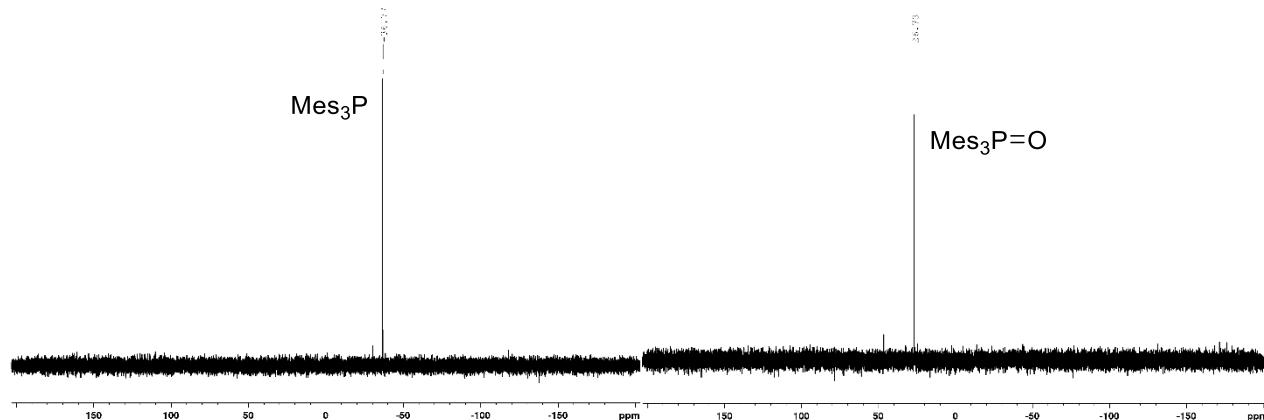
**Figure S43.** LED plate and water-cooled block (left) used to setup the irradiation setup as shown right. 455 nm irradiation depicted

## SUPPORTING INFORMATION

**7. Mes<sub>3</sub>P + B(NO<sub>2</sub>-Mes)<sub>3</sub>**

Trimesitylphosphine (9.7 mg, 0.025 mmol, 1.0 eq.) and tris(3,5-dinitromesityl)borane (16 mg, 0.025 mmol, 1.0 eq.) were added together in 1 mL DCM to yield a pale yellow solution. Two samples were prepared of which one was kept in the dark while the other was irradiated with 455 nm light (High power LEDS: OSRAM Oslon SSL 80) for 3 days using the LED-setup described above. The dark sample showed no change in <sup>31</sup>P-NMR whereas the irradiated sample shows full conversion to trimesitylphosphine oxide. As the only source of oxygen atoms in the sample is the tris(3,5-dinitromesityl)borane, we postulate that the oxygen originated from this species.

As no reaction occurs in darkness, the reaction must be light induced. We propose that light induced single-electron-transfer takes place generating the borane radical anion B(NO<sub>2</sub>-Mes)<sub>3</sub><sup>-·</sup> and phosphonium radical cation Mes<sub>3</sub>P<sup>·+</sup>. Such phosphonium radical cations are known to be highly oxophilic<sup>12</sup> which drives the subsequent reaction with the oxygen atoms on the borane radical anion. This mechanism is currently under further investigation.



**Figure S44.** <sup>31</sup>P-NMR spectra of PMes<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> after 3 days in the dark (left) and irradiated with 455 nm nm light (right)

**SUPPORTING INFORMATION****8. Computational details: Coordinates ionization potential and electron affinity calculations**

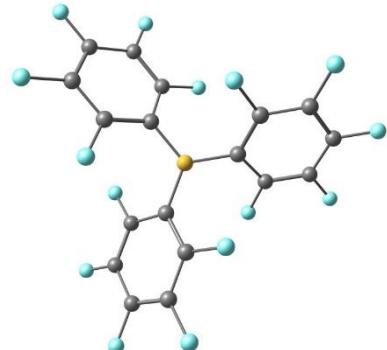
All structures in this section were optimized at  $\omega$ B97X-D/6-31G(d)<sup>2,3</sup> using Gaussian 09, Revision D01.<sup>5</sup> ZPE and Gibbs free energy corrections ( $G^\circ$ ) were obtained from frequency analyses performed at this level of theory. Energy levels were obtained from single-point calculations at the  $\omega$ B97X-D/6-311+G(d,p) level of theory. These are the geometries used in section 2.

 **$\text{B}(\text{C}_6\text{F}_5)_3$** 

E: -2207.59590223 a.u  
 ZPE: -2208.109891 a.u  
 G: -2208.171366 a.u

Cartesian coordinates:

C	0.553658	1.464996	-0.00108
C	-0.059378	2.489293	0.72559
C	0.422761	3.789373	0.74540
C	1.552671	4.104836	0.00020
C	2.190838	3.120966	-0.74565
C	1.691445	1.827396	-0.72718
F	-1.140419	2.233891	1.46558
F	-0.181675	4.729857	1.46391
F	2.021311	5.343142	0.00078
F	3.266722	3.426283	-1.46353
F	2.332756	0.920979	-1.46787
B	-0.000478	-0.000179	-0.00103
C	0.991692	-1.212363	-0.00044
C	2.185066	-1.192793	0.72659
C	3.070756	-2.259660	0.74641
C	2.780124	-3.395946	0.00081
C	1.609186	-3.457505	-0.74533
C	0.737715	-2.378941	-0.72685
F	2.503316	-0.128840	1.46700
F	4.187159	-2.205725	1.46531
F	3.619085	-4.420240	0.00133
F	1.336805	-4.542059	-1.46342
F	-0.367702	-2.481768	-1.46779
C	-1.546347	-0.253153	-0.00079
C	-2.126551	-1.297261	0.72473
C	-3.493475	-1.530125	0.74440
C	-4.332007	-0.708593	0.00044
C	-3.799442	0.337118	-0.74415
C	-2.429511	0.551686	-0.72569
F	-1.364764	-2.106379	1.46394
F	-4.005358	-2.524814	1.46179
F	-5.638676	-0.922222	0.00109
F	-4.602123	1.117015	-1.46078
F	-1.965637	1.561429	-1.46506



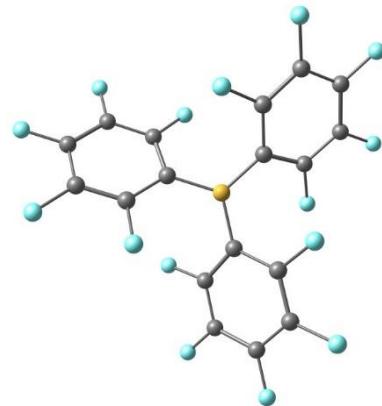
## SUPPORTING INFORMATION

**B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>\*\*</sup>**

E: -2207.66031203 a.u  
 ZPE: -2208.197675 a.u  
 G: -2208.25841 a.u

Cartesian coordinates:

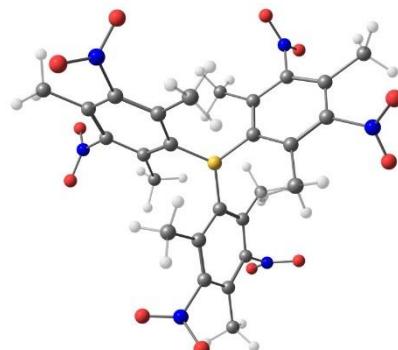
C	1.153668	-1.062999	-0.00170
C	2.380038	-0.864824	0.65185
C	3.412734	-1.789673	0.65856
C	3.256282	-3.001330	-0.00074
C	2.061577	-3.255799	-0.66046
C	1.055887	-2.301561	-0.65484
F	2.599595	0.262886	1.34784
F	4.554785	-1.537571	1.31440
F	4.241387	-3.909813	-0.00015
F	1.903174	-4.414990	-1.31545
F	-0.049996	-2.612094	-1.35143
B	-0.000115	0.000213	-0.00160
C	-1.497511	-0.467676	-0.00068
C	-1.938513	-1.628455	0.65405
C	-3.255711	-2.060689	0.66148
C	-4.227289	-1.320332	0.00180
C	-3.850858	-0.159027	-0.65928
C	-2.521742	0.235138	-0.65446
F	-1.071370	-2.381181	1.35123
F	-3.607857	-3.175220	1.31854
F	-5.506447	-1.719737	0.00312
F	-4.775966	0.556810	-1.31475
F	-2.238298	1.347577	-1.35210
C	0.343779	1.531008	-0.00086
C	-0.444109	2.494538	0.64834
C	-0.159655	3.851359	0.65503
C	0.970875	4.321417	0.00061
C	1.791780	3.413535	-0.65452
C	1.468437	2.065464	-0.64904
F	-1.533464	2.121420	1.34013
F	-0.952143	4.714819	1.30641
F	1.264725	5.628889	0.00149
F	2.877832	3.855491	-1.30494
F	2.294327	1.262531	-1.34022

**B(NO<sub>2</sub>-Mes)<sub>3</sub>**

E: -2299.86859537 a.u  
 ZPE: -2299.959533 a.u  
 G: -2300.04424 a.u

Cartesian coordinates:

B	-0.000059	0.000262	-0.00231
C	-0.181174	-1.570720	-0.00137
C	-1.070322	-2.183170	0.90563
C	-1.201860	-3.570355	0.86989
C	-0.505149	-4.409518	0.00834
C	0.358683	-3.751674	-0.86324
C	0.547144	-2.372738	-0.90680
C	-1.269831	0.942732	-0.00182
C	-1.355615	2.018902	0.90519
C	-2.491249	2.826205	0.86947
C	-3.566386	2.642345	0.00810
C	-3.428699	1.565271	-0.86337
C	-2.328636	0.712763	-0.90694
C	1.451001	0.628761	-0.00122



## SUPPORTING INFORMATION

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C	2.424950	0.166194	0.90730
C	3.692106	0.745424	0.87137
C	4.071695	1.766311	0.00811
C	3.070899	2.184481	-0.86492
C	1.782140	1.658938	-0.90788
C	-1.859082	-1.402575	1.93416
H	-1.341676	-0.491710	2.23845
H	-2.839112	-1.114992	1.54013
H	-2.024512	-1.990662	2.84035
C	1.482742	-1.787290	-1.94182
H	1.174565	-0.785446	-2.24420
H	2.504005	-1.721585	-1.55373
H	1.513405	-2.398151	-2.84713
C	2.142439	-0.905133	1.93763
H	1.094329	-0.912851	2.23991
H	2.385052	-1.898333	1.54629
H	2.732652	-0.751378	2.84453
C	0.806948	2.174999	-1.94315
H	0.091716	1.407381	-2.24209
H	0.241173	3.028522	-1.55674
H	1.319759	2.503308	-2.85031
C	-0.285157	2.311540	1.93365
H	0.243734	1.407630	2.23883
H	0.454986	3.015006	1.53898
H	-0.711347	2.750271	2.83930
C	-2.289251	-0.390596	-1.94147
H	-1.267478	-0.624753	-2.24366
H	-2.743038	-1.307755	-1.55312
H	-2.833553	-0.112010	-2.84693
C	-4.770937	3.545898	-0.01568
H	-4.688223	4.259254	-0.84100
H	-5.687708	2.970164	-0.16746
H	-4.875354	4.094710	0.92020
C	-0.684602	-5.904622	-0.01574
H	-1.117042	-6.269228	0.91587
H	-1.334621	-6.190936	-0.84777
H	0.274410	-6.410113	-0.15658
C	5.456683	2.357242	-0.01526
H	5.984856	2.170452	0.91969
H	6.032348	1.931248	-0.84225
H	5.416407	3.439548	-0.16384
N	-4.535215	1.319026	-1.79986
O	-5.160073	0.281588	-1.65916
O	-4.748128	2.168596	-2.64861
N	-2.545886	3.960008	1.80601
O	-3.297179	3.865184	2.76286
O	-1.820340	4.907146	1.56069
N	-2.156458	-4.184238	1.80659
O	-3.339477	-4.028566	1.56174
O	-1.698857	-4.788181	2.76306
N	1.125645	-4.586617	-1.79969
O	2.336479	-4.608621	-1.65855
O	0.496915	-5.194937	-2.64950
N	3.411978	3.263904	-1.80337
O	2.825131	4.323765	-1.66599
O	4.255554	3.021960	-2.65034
N	4.700243	0.227692	1.81007
O	5.157333	-0.875084	1.56792
O	4.992835	0.927774	2.76572

## SUPPORTING INFORMATION

**B(NO<sub>2</sub>-Mes)<sub>3</sub><sup>•-</sup>**

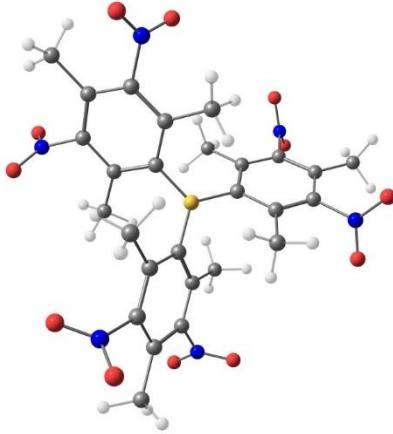
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ZPE: -2300.054751 a.u

G: -2300.138866 a.u

Cartesian coordinates:

B	0.000396	-0.000231	0.00390
C	-1.036925	-1.194490	0.00466
C	-2.192098	-1.169306	0.83118
C	-3.095970	-2.228515	0.77744
C	-2.940146	-3.374666	0.00593
C	-1.783275	-3.372102	-0.77049
C	-0.853320	-2.337126	-0.82233
C	-0.515438	1.495225	0.00406
C	0.083146	2.483320	0.83088
C	-0.383711	3.795223	0.77791
C	-1.454262	4.232754	0.00600
C	-2.028980	3.229493	-0.77141
C	-1.596572	1.906955	-0.82340
C	1.553256	-0.301495	0.00397
C	2.109628	-1.314177	0.83058
C	3.479182	-1.566117	0.77722
C	4.393440	-0.857539	0.00561
C	3.812004	0.142103	-0.77137
C	2.450529	0.428992	-0.82335
C	-2.448185	-0.044494	1.80608
H	-1.500037	0.357310	2.16995
H	-2.993569	0.781492	1.33659
H	-3.028090	-0.379613	2.67094
C	0.294954	-2.427701	-1.79956
H	0.553828	-1.429962	-2.16078
H	1.191349	-2.848776	-1.33186
H	0.049466	-3.049976	-2.66458
C	1.263695	-2.099044	1.80516
H	0.442307	-1.478869	2.17069
H	0.819964	-2.983411	1.33495
H	1.844222	-2.435402	2.66906
C	1.954024	1.468056	-1.80083
H	0.960313	1.193082	-2.16124
H	1.870805	2.455157	-1.33363
H	2.614990	1.566114	-2.66644
C	1.186249	2.142854	1.80478
H	1.059301	1.121428	2.17024
H	2.173550	2.199748	1.33356
H	1.188669	2.813568	2.66882
C	-2.247094	0.957358	-1.80148
H	-1.511343	0.234774	-2.16150
H	-3.060289	0.391217	-1.33491
H	-2.662602	1.480654	-2.66709
C	-1.933800	5.661667	-0.02307
H	-1.550021	6.179840	-0.90731
H	-3.025928	5.708167	-0.06476
H	-1.616849	6.201997	0.86974
C	-3.938641	-4.503583	-0.02381
H	-4.568389	-4.496785	0.86665
H	-4.575987	-4.432005	-0.91056
H	-3.433332	-5.473111	-0.06109
C	5.870784	-1.155866	-0.02409
H	6.180547	-1.705478	0.86552
H	6.128540	-1.741759	-0.91171
H	6.456379	-0.232476	-0.05973
N	-3.171199	3.622855	-1.60882
O	-4.253406	3.114570	-1.36248
O	-2.971675	4.439254	-2.49745
N	0.302246	4.796229	1.61075



## SUPPORTING INFORMATION

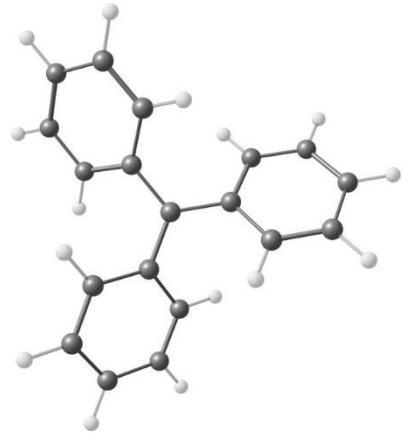
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O	-4.375739	-2.841452	2.60519
N	-1.552960	-4.558944	-1.60667
O	-0.574489	-5.244582	-1.35639
O	-2.357315	-4.792854	-2.49789
N	4.724215	0.935411	-1.60772
O	4.829064	2.125438	-1.35679
O	5.327922	0.356334	-2.50001
N	4.002908	-2.661109	1.60955
O	3.749351	-3.800378	1.25577
O	4.650931	-2.366897	2.60483

**CPh<sub>3</sub><sup>+</sup>**

E: -732.559283147 a.u  
 ZPE: -732.4418668 a.u  
 G: -732.4839428 a.u

Cartesian coordinates:

C	-1.434900	-0.168757	0.00036
C	-2.029598	-1.259964	-0.67458
C	-2.266062	0.755212	0.67523
C	-3.406100	-1.407926	-0.68444
H	-1.405123	-1.951815	-1.22980
C	-3.639450	0.580701	0.68479
H	-1.818746	1.572735	1.23059
C	-4.209422	-0.494106	0.00008
H	-3.858147	-2.230386	-1.22799
H	-4.269624	1.276311	1.22816
H	-5.287496	-0.620483	-0.00006
C	0.863315	-1.158284	0.00045
C	2.105852	-1.126601	-0.67417
C	0.479203	-2.340734	0.67446
C	2.922865	-2.244252	-0.68462
H	2.392385	-0.239223	-1.22859
C	1.317637	-3.442421	0.68341
H	-0.452459	-2.363149	1.22976
C	2.533577	-3.397528	-0.00098
H	3.861312	-2.223613	-1.22787
H	1.030699	-4.336497	1.22613
H	3.182556	-4.267620	-0.00154
C	0.571096	1.326526	0.00054
C	-0.075344	2.386266	-0.67694
C	1.785521	1.585311	0.67742
C	0.484668	3.652383	-0.68720
H	-0.985306	2.190962	-1.23429
C	2.320863	2.862068	0.68663
H	2.268894	0.789861	1.23466
C	1.676266	3.892206	-0.00055
H	-0.000546	4.454377	-1.23276
H	3.237235	3.060738	1.23163
H	2.105736	4.889090	-0.00105
C	-0.000217	-0.000314	0.00060



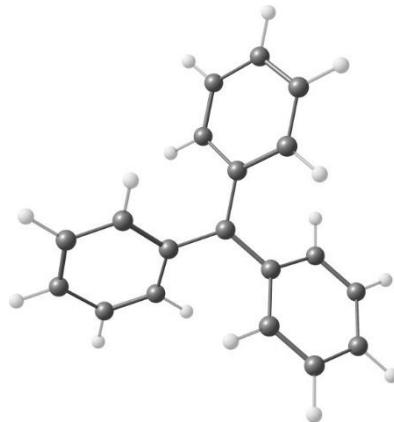
## SUPPORTING INFORMATION

**CPh<sub>3</sub><sup>•</sup>**

E: -732.773663319 a.u  
 ZPE: -732.6679641 a.u  
 G: -732.7113911 a.u

Cartesian coordinates:

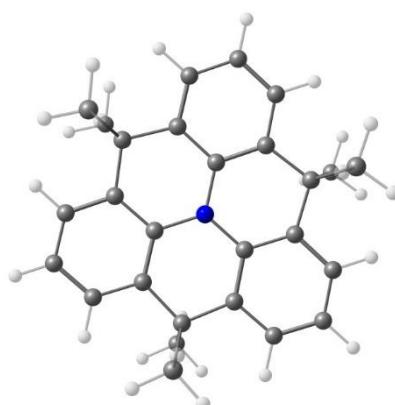
C	1.407283	-0.397786	-0.00015
C	2.381520	0.364302	-0.67609
C	1.839175	-1.556835	0.67583
C	3.716777	-0.015652	-0.67685
H	2.074789	1.252682	-1.21948
C	3.175983	-1.931293	0.67642
H	1.113123	-2.153590	1.21924
C	4.123206	-1.164598	-0.00027
H	4.444218	0.584495	-1.21586
H	3.482166	-2.823302	1.21536
H	5.168229	-1.459704	-0.00040
C	-0.359017	1.417338	-0.00022
C	-1.505045	1.880536	-0.67760
C	0.427893	2.370359	0.67746
C	-1.843529	3.226915	-0.67798
H	-2.120511	1.170977	-1.22193
C	0.083971	3.715362	0.67831
H	1.306825	2.039773	1.22218
C	-1.052588	4.152875	0.00024
H	-2.726282	3.557206	-1.21791
H	0.702697	4.426152	1.21855
H	-1.319450	5.205465	0.00043
C	-1.047978	-1.019951	-0.00005
C	-0.875408	-2.245156	-0.67526
C	-2.267971	-0.813519	0.67519
C	-1.872423	-3.211222	-0.67557
H	0.047269	-2.424543	-1.21843
C	-3.261024	-1.783636	0.67616
H	-2.421756	0.114316	1.21746
C	-3.070761	-2.987931	0.00052
H	-1.716536	-4.141716	-1.21387
H	-4.186819	-1.602002	1.21449
H	-3.849058	-3.745177	0.00074
C	0.000118	-0.000281	-0.00016

**N<sub>b</sub>Ar<sub>3</sub>**

E: -1099.62205905 a.u  
 ZPE: -1099.368136 a.u  
 G: -1099.417744 a.u

Cartesian coordinates:

C	1.349135	0.440217	-0.00001
C	1.661964	1.814176	0.00010
C	2.995213	2.221089	0.00011
H	3.218811	3.282464	0.00021
C	4.040326	1.318058	0.00000
H	5.071394	1.654328	0.00000
C	3.728707	-0.027512	-0.00010
H	4.535063	-0.753054	-0.00018
C	2.412034	-0.484894	-0.00011
C	2.214940	-1.989258	-0.00021
C	0.740157	-2.346357	-0.00020
C	0.426215	-3.704422	-0.00027
H	1.233755	-4.428600	-0.00031
C	-0.878305	-4.158184	-0.00027
H	-1.102404	-5.219304	-0.00031



## SUPPORTING INFORMATION

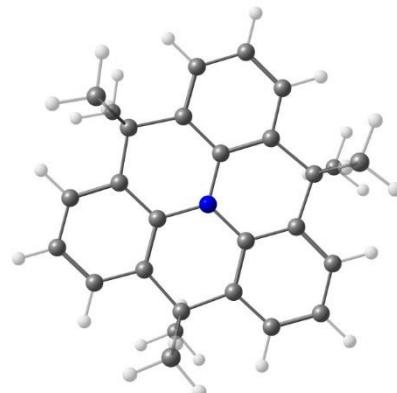
C	-1.887968	-3.215719	-0.00020
H	-2.919341	-3.551617	-0.00020
C	-1.626083	-1.846627	-0.00013
C	-0.293470	-1.388638	-0.00012
C	-2.830473	-0.923610	-0.00006
C	-2.402249	0.532130	0.00005
C	-3.421275	1.483239	0.00018
H	-4.452253	1.146142	0.00017
C	-3.161836	2.839819	0.00032
H	-3.968664	3.564548	0.00043
C	-1.840749	3.242825	0.00034
H	-1.615716	4.303914	0.00046
C	-0.786171	2.331341	0.00020
C	-1.055990	0.948303	0.00007
C	0.615396	2.912855	0.00025
C	0.798846	3.781200	1.26772
H	1.794766	4.230770	1.30010
H	0.069322	4.594655	1.30012
H	0.670353	3.171980	2.16652
C	0.798819	3.781523	-1.26698
H	0.670290	3.172535	-2.16593
H	0.069311	4.595000	-1.29915
H	1.794743	4.231089	-1.29928
C	2.875578	-2.582114	1.26707
H	2.412200	-2.166429	2.16594
H	2.767108	-3.669399	1.29932
H	3.944834	-2.356940	1.29949
C	2.875531	-2.581942	-1.26760
H	3.944783	-2.356755	-1.30003
H	2.767073	-3.669224	-1.29999
H	2.412111	-2.166145	-2.16640
C	-3.674192	-1.198791	-1.26757
H	-3.082020	-1.006132	-2.16630
H	-4.014944	-2.236958	-1.30000
H	-4.560988	-0.560446	-1.30040
C	-3.674201	-1.198997	1.26739
H	-4.560999	-0.560660	1.30032
H	-4.014952	-2.237171	1.29965
H	-3.082037	-1.006484	2.16615
N	-0.000139	-0.000052	-0.00002

**N<sub>b</sub>Ar<sub>3</sub><sup>•+</sup>**

E: -1099.39315488 a.u  
 ZPE: -1099.130798 a.u  
 G: -1099.181115 a.u

## Cartesian coordinates:

C	1.379269	0.338996	-0.00000
C	1.787100	1.695528	0.00010
C	3.143649	1.997860	0.00008
H	3.453314	3.035703	0.00018
C	4.112124	1.010940	-0.00005
H	5.164909	1.269771	-0.00007
C	3.711800	-0.312574	-0.00015
H	4.467551	-1.088358	-0.00025
C	2.369701	-0.673781	-0.00012
C	2.062464	-2.149892	-0.00021
C	0.574826	-2.395555	-0.00017
C	0.158270	-3.721509	-0.00023
H	0.901961	-4.508843	-0.00028
C	-1.180684	-4.066672	-0.00023
H	-1.482935	-5.107820	-0.00028
C	-2.126675	-3.058173	-0.00017
H	-3.176412	-3.324700	-0.00019



## SUPPORTING INFORMATION

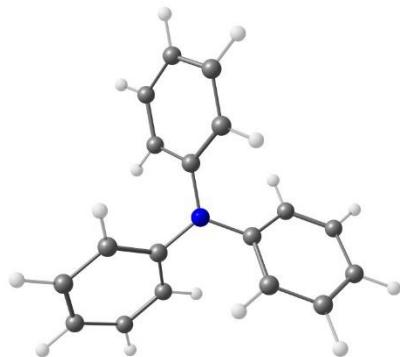
C	-1.768382	-1.715307	-0.00011
C	-0.396061	-1.364038	-0.00009
C	-2.893120	-0.711150	-0.00006
C	-2.362051	0.699993	0.00005
C	-3.302108	1.723690	0.00014
H	-4.355802	1.473356	0.00010
C	-2.931596	3.055846	0.00029
H	-3.682148	3.838160	0.00036
C	-1.585236	3.370877	0.00033
H	-1.291196	4.413244	0.00045
C	-0.601390	2.389145	0.00022
C	-0.983290	1.025031	0.00009
C	0.830617	2.861048	0.00027
C	1.077905	3.711205	1.27323
H	2.103266	4.084827	1.30105
H	0.414006	4.577346	1.30057
H	0.904647	3.117674	2.17451
C	1.077881	3.711577	-1.27243
H	0.904600	3.118311	-2.17388
H	0.413993	4.577733	-1.29951
H	2.103241	4.085206	-1.30016
C	2.675561	-2.789135	1.27252
H	2.247717	-2.343129	2.17398
H	2.487574	-3.864136	1.29986
H	3.757468	-2.646192	1.29990
C	2.675463	-2.788979	-1.27306
H	3.757368	-2.646033	-1.30051
H	2.487474	-3.863976	-1.30052
H	2.247549	-2.342863	-2.17444
C	-3.753091	-0.922342	-1.27293
H	-3.152859	-0.774343	-2.17429
H	-4.169928	-1.930899	-1.30074
H	-4.590281	-0.222252	-1.30015
C	-3.753182	-0.922532	1.27270
H	-4.590373	-0.222446	1.29997
H	-4.170029	-1.931089	1.30033
H	-3.153013	-0.774672	2.17412
N	-0.000034	-0.000024	-0.00000

**NPh<sub>3</sub>**

E: -749.436354107 a.u  
 ZPE: -749.336973 a.u  
 G: -749.380561 a.u

Cartesian coordinates:

N	0.000013	0.000059	0.00018
C	-1.056378	0.942011	0.00007
C	-2.192260	0.732611	-0.78976
C	-0.978160	2.094456	0.78980
C	-3.231957	1.655259	-0.77845
H	-2.255019	-0.157830	-1.40728
C	-2.013533	3.021956	0.77831
H	-0.100797	2.258548	1.40743
C	-3.148299	2.807198	-0.00011
H	-4.107893	1.476982	-1.39547
H	-1.936552	3.912563	1.39529
H	-3.958557	3.529608	-0.00017
C	-0.287562	-1.385789	0.00010
C	0.461409	-2.264760	-0.79004
C	-1.324453	-1.894265	0.79017
C	0.182117	-3.626485	-0.77879
H	1.263750	-1.873875	-1.40779
C	-1.610101	-3.254665	0.77865
H	-1.905011	-1.216497	1.40802



## SUPPORTING INFORMATION

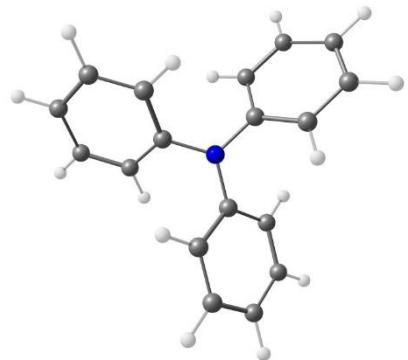
C	-0.857077	-4.129990	-0.00014
H	0.774186	-4.295905	-1.39611
H	-2.419688	-3.633301	1.39587
H	-1.077689	-5.192878	-0.00024
C	1.343996	0.443885	0.00008
C	1.730751	1.532029	-0.79002
C	2.302775	-0.199961	0.79009
C	3.049689	1.970983	-0.77868
H	0.991099	2.031460	-1.40779
C	3.623745	0.232819	0.77864
H	2.006022	-1.041656	1.40786
C	4.005312	1.322689	-0.00005
H	3.333445	2.818479	-1.39593
H	4.356431	-0.279069	1.39581
H	5.036106	1.663074	-0.00011

**NPh<sub>3</sub><sup>•+</sup>**

E: -749.196260414 a.u  
 ZPE: -749.0868281 a.u  
 G: -749.1299581 a.u

Cartesian coordinates:

N	0.000077	-0.000142	-0.00047
C	-1.008975	-0.981042	-0.00022
C	-2.173866	-0.781341	0.76092
C	-0.842716	-2.151319	-0.76113
C	-3.160240	-1.754167	0.75814
H	-2.277643	0.110948	1.36891
C	-1.843326	-3.109470	-0.75801
H	0.045984	-2.280659	-1.36946
C	-2.999819	-2.915822	0.00014
H	-4.052892	-1.613657	1.35784
H	-1.728465	-4.005839	-1.35761
H	-3.777858	-3.671937	0.00024
C	-0.344940	1.364144	-0.00030
C	0.410140	2.273119	0.76113
C	-1.441484	1.805249	-0.76135
C	0.060457	3.613640	0.75874
H	1.234792	1.916929	1.36916
C	-1.771341	3.150796	-0.75788
H	-1.997534	1.100254	-1.36994
C	-1.025816	4.055479	0.00075
H	0.628152	4.316402	1.35878
H	-2.605067	3.499468	-1.35749
H	-1.291962	5.107246	0.00121
C	1.354102	-0.383432	-0.00036
C	1.764037	-1.491561	0.76132
C	2.284161	0.345538	-0.76178
C	3.099848	-1.858921	0.75865
H	1.043469	-2.027365	1.36983
C	3.614387	-0.041531	-0.75862
H	1.951478	1.179448	-1.37048
C	4.025370	-1.139327	0.00013
H	3.424813	-2.701760	1.35884
H	4.333010	0.506031	-1.35858
H	5.069303	-1.434712	0.00035



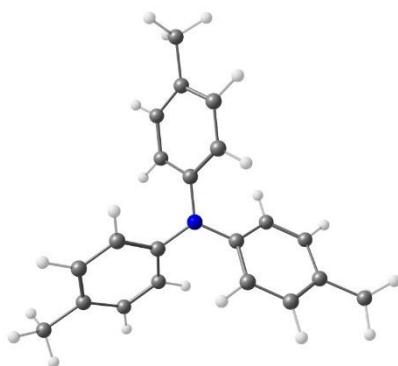
## SUPPORTING INFORMATION

**NpTol<sub>3</sub>**

E: -867.354769896 a.u  
 ZPE: -867.2002348 a.u  
 G: -867.2536238 a.u

Cartesian coordinates:

N	0.000234	0.002061	0.00231
C	1.299825	0.562092	-0.00034
C	1.596048	1.677201	-0.78791
C	2.313828	0.011115	0.79159
C	2.872420	2.229054	-0.77221
H	0.819311	2.115957	-1.40646
C	3.588603	0.559421	0.77982
H	2.095186	-0.850911	1.41412
C	3.894910	1.680091	0.00210
H	3.077381	3.100351	-1.38971
H	4.360995	0.114462	1.40330
C	-1.134939	0.847007	-0.00069
C	-2.248837	0.542138	-0.78904
C	-1.163298	2.005906	0.78119
C	-3.363059	1.372200	-0.78045
H	-2.236722	-0.350162	-1.40718
C	-2.275742	2.837899	0.76257
H	-0.304482	2.255875	1.39627
C	-3.399992	2.535986	-0.00927
H	-4.217490	1.114622	-1.40207
H	-2.273141	3.736893	1.37458
C	-0.164255	-1.403133	0.00232
C	0.662290	-2.218200	-0.77690
C	-1.153730	-2.005380	0.78636
C	0.504274	-3.598724	-0.76006
H	1.435354	-1.764907	-1.38940
C	-1.314273	-3.385203	0.77538
H	-1.796912	-1.384868	1.40272
C	-0.489404	-4.210144	0.00686
H	1.162888	-4.212536	-1.37007
H	-2.089770	-3.831305	1.39369
C	-4.621047	3.421166	0.01103
H	-5.171371	3.363841	-0.93363
H	-5.311080	3.124697	0.81079
H	-4.352339	4.468654	0.18196
C	5.288785	2.256485	-0.00738
H	5.685358	2.357526	1.00885
H	5.980402	1.612460	-0.56417
H	5.308546	3.245202	-0.47574
C	-0.684873	-5.705526	-0.01416
H	-1.055450	-6.073477	0.94820
H	-1.414437	-5.997887	-0.77963
H	0.250940	-6.227617	-0.23746



## SUPPORTING INFORMATION

**NpTol<sub>3</sub><sup>•+</sup>**

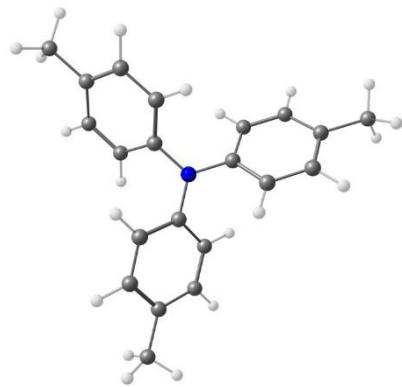
E: -867.126001142 a.u

ZPE: -866.9630164 a.u

G: -867.0144524 a.u

Cartesian coordinates:

N	-0.001825	-0.002380	0.00183
C	-1.345132	-0.417101	0.00312
C	-2.296854	0.286813	0.76005
C	-1.736232	-1.536885	-0.75034
C	-3.614707	-0.133512	0.75885
H	-1.988827	1.131152	1.36759
C	-3.060953	-1.934251	-0.74246
H	-1.006980	-2.064039	-1.35625
C	-4.024906	-1.244978	0.00816
H	-4.341688	0.401242	1.36254
H	-3.360716	-2.790562	-1.33904
C	0.310457	1.368581	0.00288
C	1.397455	1.841070	0.75747
C	-0.465937	2.267096	-0.74815
C	1.691639	3.192600	0.75628
H	1.976370	1.152211	1.36343
C	-0.148355	3.613313	-0.74046
H	-1.288575	1.899015	-1.35197
C	0.931957	4.103636	0.00772
H	2.519362	3.554983	1.35834
H	-0.741929	4.300990	-1.33525
C	1.029995	-0.957438	-0.00145
C	0.898898	-2.137497	0.74991
C	2.192087	-0.733065	-0.75879
C	1.921569	-3.068806	0.73957
H	0.013914	-2.298704	1.35626
C	3.198461	-1.681883	-0.76002
H	2.278972	0.162471	-1.36485
C	3.088184	-2.862899	-0.01131
H	1.821803	-3.971602	1.33455
H	4.084810	-1.513145	-1.36406
C	1.283181	5.564627	-0.01361
H	1.755863	5.876331	0.92167
H	1.990650	5.771204	-0.82585
H	0.399736	6.186767	-0.18024
C	-5.465723	-1.671380	-0.01386
H	-5.992170	-1.180687	-0.84150
H	-5.561439	-2.751067	-0.15738
H	-5.978944	-1.397389	0.91171
C	4.203611	-3.869759	0.00728
H	4.764249	-3.863252	-0.93134
H	4.908815	-3.637327	0.81449
H	3.827323	-4.881629	0.17986

**PMes<sub>3</sub>**

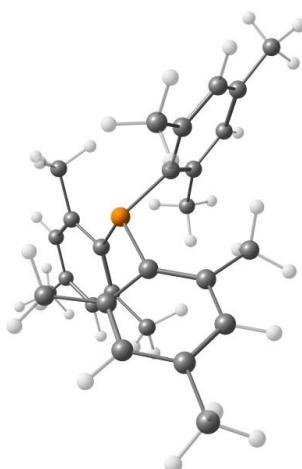
E: -1389.77576852 a.u

ZPE: -1389.526732 a.u

G: -1389.588717 a.u

Cartesian coordinates:

C	-1.540148	0.799661	-0.24153
C	-1.649075	1.773216	0.77540
C	-2.703500	0.433040	-0.96229
C	-2.892221	2.360932	1.02291
C	-3.924436	1.033558	-0.66224
C	-4.040005	2.013418	0.31911



## SUPPORTING INFORMATION

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H	-2.965171	3.107524	1.81141
H	-4.810066	0.728411	-1.21611
C	1.462501	0.934444	-0.24130
C	2.360964	0.540379	0.77462
C	1.726294	2.125931	-0.96047
C	3.492084	1.322073	1.02160
C	2.857513	2.882156	-0.66037
C	3.764951	2.490535	0.31889
H	4.175710	1.010995	1.80923
H	3.035592	3.802322	-1.21330
C	0.077429	-1.733150	-0.24193
C	-0.712202	-2.314385	0.77441
C	0.976863	-2.557218	-0.96190
C	-0.600135	-3.684870	1.02140
C	1.067189	-3.914964	-0.66169
C	0.275523	-4.505159	0.31859
H	-1.210506	-4.121733	1.80942
H	1.774901	-4.529109	-1.21506
P	-0.000029	0.000519	-0.86021
C	0.789254	2.643088	-2.02715
H	0.623162	1.895979	-2.81091
H	-0.195483	2.892327	-1.61406
H	1.195299	3.547147	-2.49024
C	2.159450	-0.663060	1.66517
H	1.140362	-0.713541	2.05780
H	2.340759	-1.606590	1.14122
H	2.844377	-0.615511	2.51702
C	5.007751	3.296847	0.59643
H	5.353394	3.157184	1.62553
H	5.825480	2.994840	-0.06944
H	4.833822	4.365916	0.43730
C	-0.506527	2.199661	1.66670
H	0.048166	1.342366	2.05738
H	0.218406	2.831327	1.14424
H	-0.891031	2.766440	2.51985
C	-5.360281	2.685277	0.59743
H	-5.508312	3.545238	-0.06727
H	-6.198606	1.999544	0.43747
H	-5.412391	3.053006	1.62704
C	-2.681680	-0.636138	-2.02979
H	-1.949735	-0.406686	-2.81180
H	-2.406619	-1.613893	-1.61642
H	-3.666877	-0.735315	-2.49470
C	-1.653270	-1.538062	1.66540
H	-1.186014	-0.631972	2.06051
H	-2.560296	-1.220806	1.14169
H	-1.956249	-2.156037	2.51581
C	1.891992	-2.003720	-2.02922
H	1.326836	-1.487648	-2.81300
H	2.599219	-1.274190	-1.61683
H	2.472821	-2.806889	-2.49206
C	0.353614	-5.984350	0.59743
H	0.070090	-6.211912	1.62983
H	-0.324249	-6.541788	-0.06062
H	1.364321	-6.369584	0.42861

## SUPPORTING INFORMATION

**PMes<sub>3</sub><sup>•+</sup>**

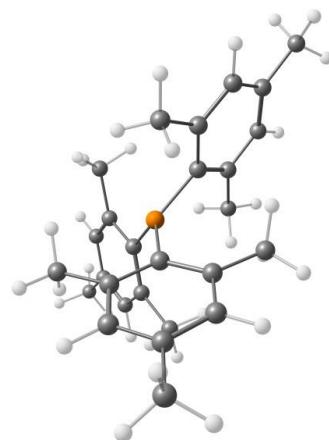
E: -1389.55085210 a.u

ZPE: -1389.296722 a.u

G: -1389.361631 a.u

Cartesian coordinates:

C	-0.351725	1.724314	0.12666
C	-1.277616	2.167291	-0.85038
C	0.331630	2.648448	0.95658
C	-1.487291	3.536566	-0.97339
C	0.081797	4.003744	0.78020
C	-0.825793	4.469495	-0.17281
H	-2.183809	3.891250	-1.72856
H	0.603283	4.720070	1.40953
C	-1.317524	-1.166896	0.12690
C	-1.238237	-2.189996	-0.85039
C	-2.459654	-1.037235	0.95683
C	-2.319144	-3.056288	-0.97343
C	-3.508432	-1.931209	0.78023
C	-3.457919	-2.949962	-0.17290
H	-2.278049	-3.836652	-1.72881
H	-4.389609	-1.837858	1.40946
C	1.669228	-0.557707	0.12681
C	2.515233	0.022363	-0.85083
C	2.128485	-1.611322	0.95697
C	3.805995	-0.480409	-0.97411
C	3.427157	-2.072222	0.78017
C	4.283830	-1.519262	-0.17336
H	4.461053	-0.054532	-1.72963
H	3.787331	-2.881591	1.40972
P	-0.000013	-0.000115	0.38730
C	-2.580984	0.038807	2.00881
H	-1.698029	0.079307	2.65759
H	-2.704331	1.030903	1.56012
H	-3.448289	-0.146069	2.64646
C	-0.064546	-2.365377	-1.78289
H	0.243536	-1.420710	-2.24336
H	0.810508	-2.773009	-1.26630
H	-0.325489	-3.054571	-2.58907
C	-4.593036	-3.925685	-0.31691
H	-4.665917	-4.307210	-1.33896
H	-4.438721	-4.784980	0.34647
H	-5.549552	-3.469405	-0.04785
C	-2.017489	1.238787	-1.78218
H	-1.355057	0.496839	-2.24046
H	-2.810576	0.688380	-1.26565
H	-2.481114	1.809210	-2.59006
C	-1.103358	5.940440	-0.31618
H	-1.921944	6.236847	0.35039
H	-0.228712	6.540436	-0.05059
H	-1.401197	6.194258	-1.33711
C	1.324452	2.214903	2.00800
H	0.918891	1.428651	2.65568
H	2.245411	1.826867	1.55846
H	1.597539	3.057719	2.64683
C	2.080391	1.127032	-1.78270
H	1.105207	0.925235	-2.23834
H	2.002752	2.089589	-1.26678
H	2.804533	1.241763	-2.59233
C	1.257887	-2.254678	2.00938
H	0.781638	-1.510945	2.65913
H	0.460242	-2.857585	1.56097
H	1.852147	-2.913597	2.64631
C	5.696600	-2.013917	-0.31711
H	6.064296	-1.884404	-1.33861



## SUPPORTING INFORMATION

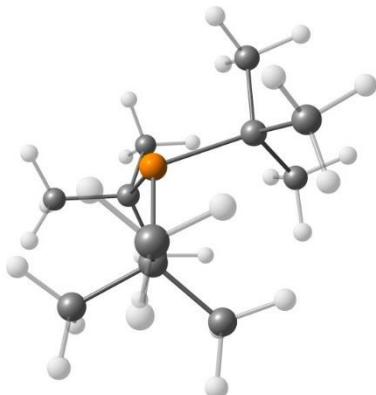
H	6.362931	-1.451739	0.34789
H	5.779674	-3.070879	-0.04984

**PtBu<sub>3</sub>**

E: -814.732922199 a.u  
 ZPE: -814.5135309 a.u  
 G: -814.5542979 a.u

Cartesian coordinates:

P	-0.000007	-0.000091	-0.71393
C	0.746102	-1.625766	-0.00571
C	2.271755	-1.621507	-0.22079
C	0.473226	-1.951481	1.47073
C	0.222971	-2.783467	-0.88493
H	2.536089	-1.370439	-1.25362
H	2.795293	-0.937821	0.45085
H	2.658516	-2.628465	-0.01771
H	-0.587191	-2.125231	1.66963
H	1.006075	-2.872321	1.74527
H	0.816794	-1.159722	2.14132
H	0.738118	-3.710821	-0.60082
H	-0.846405	-2.963418	-0.77467
H	0.426554	-2.595171	-1.94429
C	1.034993	1.458941	-0.00576
C	1.453384	1.386004	1.47079
C	2.299378	1.584396	-0.88476
C	0.268530	2.778017	-0.22131
H	0.595867	1.288322	2.14136
H	2.133807	0.554481	1.67043
H	1.984641	2.307901	1.74486
H	2.034769	1.666226	-1.94420
H	2.844885	2.494277	-0.60083
H	2.989893	0.748295	-0.77405
H	0.947269	3.616540	-0.01883
H	-0.081422	2.880916	-1.25407
H	-0.585099	2.889963	0.45054
C	-1.781075	0.166754	-0.00579
C	-2.540293	-1.156614	-0.22087
C	-1.927072	0.566019	1.47062
C	-2.521855	1.198778	-0.88505
H	-2.455015	-1.511150	-1.25368
H	-2.210110	-1.951901	0.45079
H	-3.605730	-0.988038	-0.01784
H	-1.547040	1.571075	1.66976
H	-2.991090	0.565364	1.74469
H	-1.413761	-0.127597	2.14143
H	-3.582690	1.216127	-0.60146
H	-2.143148	2.214834	-0.77422
H	-2.460021	0.928718	-1.94448



## SUPPORTING INFORMATION

**PtBu<sub>3</sub><sup>++</sup>**

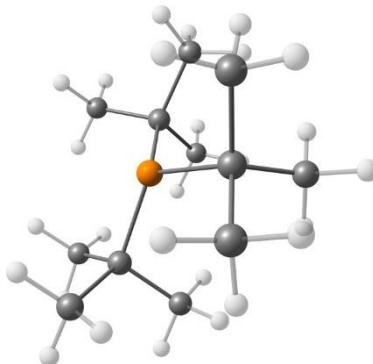
E: -814.483394747 a.u

ZPE: -814.2595097 a.u

G: -814.3020367 a.u

Cartesian coordinates:

P	0.000128	-0.000122	-0.41324
C	-0.330240	1.817491	-0.02122
C	-1.811671	2.171381	-0.23996
C	0.051350	2.106003	1.44527
C	0.489928	2.698125	-0.98854
H	-2.132950	1.994446	-1.27001
H	-2.486459	1.655103	0.44473
H	-1.920952	3.243581	-0.04602
H	1.113900	1.955577	1.64698
H	-0.170449	3.160172	1.64757
H	-0.527870	1.505694	2.15271
H	0.201776	3.740250	-0.81387
H	1.565274	2.632753	-0.83316
H	0.269257	2.468114	-2.03567
C	-1.409118	-1.194742	-0.02116
C	-1.850046	-1.008116	1.44517
C	-2.581460	-0.924474	-0.98886
C	-0.975404	-2.654866	-0.23957
H	-1.040633	-1.209294	2.15283
H	-2.251325	-0.012711	1.64637
H	-2.652025	-1.727334	1.64750
H	-2.271565	-1.000694	-2.03587
H	-3.340149	-1.694867	-0.81437
H	-3.062218	0.039680	-0.83366
H	-1.849741	-3.285198	-0.04624
H	-0.660889	-2.844765	-1.26942
H	-0.191630	-2.981655	0.44565
C	1.739472	-0.622853	-0.02124
C	2.786706	0.483107	-0.23993
C	1.798524	-1.097514	1.44531
C	2.091821	-1.773412	-0.98866
H	2.793138	0.850752	-1.26966
H	2.677832	1.324998	0.44564
H	3.769986	0.041297	-0.04725
H	1.137819	-1.943166	1.64696
H	2.822624	-1.431563	1.64790
H	1.567391	-0.295909	2.15268
H	3.138012	-2.045918	-0.81319
H	1.496610	-2.671594	-0.83432
H	2.004142	-1.466709	-2.03572



## SUPPORTING INFORMATION

**9. Computational details: Coordinates TD-DFT**

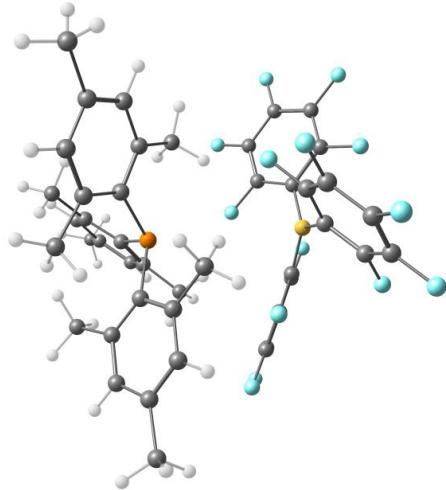
All structures in this section were optimized at  $\omega$ B97X-D/6-311G(d,p)<sup>2,3</sup> using Gaussian 09, Revision D01.<sup>5</sup> ZPE and Gibbs free energies ( $G^\circ$ ) were obtained from frequency analyses performed at the same level of theory. TD-DFT analyses were performed at the  $\omega$ B97X-D/6-311++G(d,p) level of theory. In all cases no solvent was taken into account. These are the geometries used in section 2.

**PMes<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> encounter complex**

E: -3598.28499559 a.u  
 ZPE: -3597.600393 a.u  
 G: -3597.699075 a.u

## Cartesian coordinates:

C	-0.447120	3.474793	-1.66288
C	-1.166281	2.460249	-1.05746
B	-2.317300	0.136639	-1.02115
C	-1.636849	1.340293	-1.75145
C	-1.394782	1.340567	-3.12785
C	-3.095287	0.372897	0.32387
C	-3.990703	1.426207	0.48040
C	-4.658221	1.670493	1.66618
C	-4.423194	0.845423	2.75653
C	-3.539236	-0.216009	2.64515
C	-2.911353	-0.445414	1.43388
C	-0.698904	2.348287	-3.76733
C	-2.209338	-1.332664	-1.56236
C	-3.259753	-2.238956	-1.40629
C	-3.170042	-3.566820	-1.78227
C	-1.984911	-4.037866	-2.32623
C	-0.917945	-3.173786	-2.50978
C	-1.050979	-1.846131	-2.14580
C	-0.212790	3.414464	-3.02622
C	3.250016	-0.555746	-0.50234
C	3.100481	0.084814	-1.75375
C	4.289821	-1.495854	-0.34576
C	3.941251	-0.245402	-2.81034
C	5.095732	-1.803040	-1.44169
C	4.936274	-1.204739	-2.68343
H	3.810305	0.263982	-3.76090
H	5.891802	-2.530253	-1.30878
C	2.166524	1.524921	1.38766
C	1.041446	2.045498	2.06719
C	3.274400	2.367182	1.16498
C	1.007926	3.387556	2.42444
C	3.184254	3.710539	1.52905
C	2.057500	4.249226	2.13424
H	0.128815	3.770796	2.93436
H	4.038748	4.355072	1.34205
C	1.985924	-1.371504	2.10699
C	1.345368	-2.601465	1.84024
C	2.508513	-1.140898	3.39429
C	1.224535	-3.552172	2.84665
C	2.342920	-2.117214	4.37623
C	1.701534	-3.323229	4.13125
H	0.738395	-4.496894	2.62041
H	2.750618	-1.930786	5.36586
P	1.919919	-0.168607	0.71453
C	2.092915	1.180917	-1.97750
H	1.114774	0.901480	-1.58431
H	2.388684	2.105950	-1.47067
H	1.995723	1.395421	-3.04332
C	5.801281	-1.590282	-3.85303
H	5.963520	-0.743407	-4.52358
H	6.775622	-1.957258	-3.52321
H	5.327295	-2.386649	-4.43564



## SUPPORTING INFORMATION

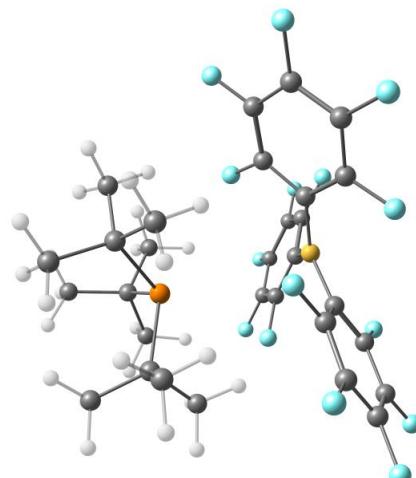
C	4.642934	-2.167052	0.95879
H	4.686619	-1.452239	1.78149
H	3.922582	-2.936090	1.24466
H	5.622732	-2.640365	0.87465
C	3.291310	0.089010	3.78119
H	4.015224	0.369437	3.01497
H	2.647913	0.958299	3.93695
H	3.836551	-0.095670	4.70852
C	0.800677	-2.934053	0.47440
H	0.002024	-2.238876	0.21075
H	1.563717	-2.864410	-0.30652
H	0.394375	-3.947438	0.46072
C	1.514293	-4.343409	5.22184
H	1.567804	-5.360630	4.82725
H	2.272969	-4.237842	6.00017
H	0.534483	-4.224455	5.69519
C	4.597140	1.902202	0.60526
H	4.884979	0.924630	0.99387
H	4.587518	1.814238	-0.48379
H	5.378440	2.615504	0.87422
C	-0.109994	1.167101	2.48109
H	-0.395267	0.486196	1.67676
H	0.161003	0.540166	3.33673
H	-0.977718	1.768189	2.75693
C	1.967570	5.716643	2.45416
H	1.409500	5.889723	3.37722
H	2.958174	6.163053	2.56382
H	1.449565	6.249199	1.65020
F	0.013930	-1.072614	-2.33423
F	0.223901	-3.627756	-3.00982
F	-1.874849	-5.309497	-2.67122
F	-4.198878	-4.390778	-1.62414
F	-1.371520	2.589008	0.24924
F	-4.424593	-1.838097	-0.89435
F	-3.301335	-0.994575	3.69289
F	-5.512982	2.680656	1.77373
F	-5.043434	1.073305	3.90295
F	-4.239118	2.244729	-0.54426
F	-2.062157	-1.474355	1.38058
F	0.021256	4.493277	-0.95469
F	-0.467522	2.294836	-5.07370
F	-1.843761	0.345995	-3.89126
F	0.484513	4.366355	-3.62089

**PtBu<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> encounter complex**

E: -3023.12633110 a.u  
 ZPE: -3022.595895 a.u  
 G: -3022.673845 a.u

## Cartesian coordinates:

C	-2.361729	3.007434	-0.73430
C	-1.829448	1.733786	-0.81275
B	0.002536	0.009473	-1.46981
C	-0.638428	1.445081	-1.47807
C	-0.038039	2.525170	-2.12512
C	-0.920448	-1.263013	-1.49661
C	-2.152425	-1.275480	-2.15051
C	-3.011703	-2.359494	-2.12157
C	-2.646349	-3.496181	-1.41809
C	-1.419234	-3.542404	-0.77609
C	-0.580093	-2.445441	-0.84036
C	-0.548897	3.810377	-2.08141
C	1.565997	-0.152679	-1.48609
C	2.198351	-1.206450	-2.14562
C	3.566824	-1.407772	-2.10875



## SUPPORTING INFORMATION

C	4.362617	-0.528640	-1.39136
C	3.783524	0.550742	-0.74356
C	2.414183	0.728080	-0.81582
C	-1.712923	4.053873	-1.36988
P	-0.002721	-0.016513	2.41663
F	1.923323	1.790257	-0.17786
F	4.542820	1.399941	-0.06087
F	5.671031	-0.709824	-1.33842
F	4.121647	-2.427674	-2.75198
F	-2.507750	0.772341	-0.18665
F	1.487373	-2.075319	-2.86501
F	-1.061512	-4.632018	-0.10631
F	-4.175289	-2.321905	-2.75911
F	-3.458372	-4.538378	-1.37279
F	-2.553053	-0.216640	-2.85516
F	0.588127	-2.559780	-0.20914
F	-3.481431	3.234626	-0.05720
F	0.060801	4.806170	-2.71268
F	1.074950	2.350562	-2.83848
F	-2.211260	5.276905	-1.31091
C	1.736715	-0.422299	3.12928
C	2.672883	0.787190	2.95938
C	1.805894	-0.862509	4.59878
C	2.337646	-1.531184	2.24147
H	2.656588	1.184315	1.94538
H	2.449105	1.600625	3.64868
H	3.698138	0.463163	3.16770
H	1.293652	-1.807346	4.77946
H	2.856046	-1.008571	4.87773
H	1.387841	-0.116373	5.27513
H	3.372600	-1.713354	2.55236
H	1.804943	-2.476859	2.30789
H	2.346665	-1.231790	1.19138
C	-1.220692	-1.328276	3.12057
C	-0.642337	-2.742118	2.93295
C	-1.629702	-1.184035	4.59350
C	-2.485673	-1.285099	2.23915
H	-0.295032	-2.916581	1.91543
H	0.176470	-2.962665	3.61695
H	-1.435142	-3.469665	3.13718
H	-2.191982	-0.270685	4.78607
H	-2.279358	-2.023893	4.86660
H	-0.771535	-1.201505	5.26584
H	-3.158930	-2.094132	2.54435
H	-3.038844	-0.352298	2.31826
H	-2.235872	-1.430886	1.18620
C	-0.526349	1.686375	3.14140
C	-2.040671	1.893804	2.96332
C	-0.189529	1.953144	4.61556
C	0.139212	2.769418	2.26794
H	-2.369866	1.690291	1.94525
H	-2.637321	1.287212	3.64372
H	-2.273989	2.941860	3.17940
H	0.883548	1.981949	4.80277
H	-0.591082	2.932600	4.90092
H	-0.629580	1.211596	5.28291
H	-0.221808	3.753934	2.58633
H	1.224251	2.779880	2.34039
H	-0.119082	2.637733	1.21519

## SUPPORTING INFORMATION

**PMes<sub>3</sub>**

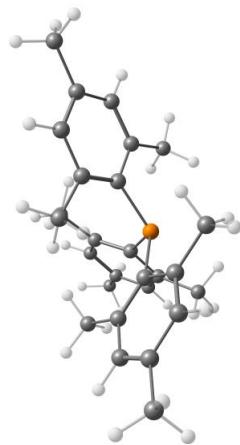
E: -1390.05046837 a.u

ZPE: -1389.524672 a.u

G: -1389.586392 a.u

Cartesian coordinates:

C	-0.404336	-1.685938	0.23806
C	0.261514	-2.405576	-0.77464
C	-1.441846	-2.321721	0.95766
C	-0.104684	-3.728899	-1.01671
C	-1.782828	-3.637532	0.66294
C	-1.116463	-4.367139	-0.31269
H	0.412368	-4.273580	-1.80187
H	-2.591971	-4.105291	1.21678
C	1.662699	0.492945	0.23779
C	1.952549	1.428220	-0.77606
C	2.732342	-0.086168	0.95821
C	3.281550	1.773023	-1.01869
C	4.042167	0.276487	0.66282
C	4.340423	1.217204	-0.31413
H	3.494347	2.492218	-1.80480
H	4.852103	-0.189339	1.21712
C	-1.257745	1.193391	0.23787
C	-2.212810	0.976494	-0.77577
C	-1.291183	2.409252	0.95829
C	-3.176375	1.954661	-1.01807
C	-2.260732	3.361844	0.66337
C	-3.224800	3.149423	-0.31326
H	-3.905751	1.779141	-1.80400
H	-2.262494	4.296115	1.21779
P	0.000341	0.000199	0.85698
C	2.507508	-1.135085	2.01918
H	1.812874	-0.781854	2.78597
H	2.073038	-2.046643	1.59629
H	3.450734	-1.403208	2.49802
C	0.912503	2.058397	-1.66883
H	0.211471	1.319751	-2.06056
H	0.316328	2.810235	-1.14701
H	1.398033	2.543593	-2.51744
C	5.761309	1.632972	-0.58666
H	5.887025	1.965508	-1.61940
H	6.052458	2.462481	0.06571
H	6.457414	0.811025	-0.40495
C	1.328524	-1.821059	-1.66671
H	1.039958	-0.845098	-2.06012
H	2.277047	-1.680042	-1.14386
H	1.507004	-2.485187	-2.51427
C	-1.466799	-5.805691	-0.58451
H	-0.890289	-6.472482	0.06470
H	-2.525626	-5.998676	-0.39801
H	-1.246200	-6.079952	-1.61847
C	-2.238903	-1.601229	2.01686
H	-1.586023	-1.172123	2.78165
H	-2.813064	-0.771799	1.59148
H	-2.940940	-2.284012	2.49829
C	-2.238410	-0.239267	-1.66861
H	-1.247718	-0.479050	-2.05779
H	-2.594598	-1.130763	-1.14765
H	-2.898927	-0.060164	-2.51887
C	-0.269893	2.739202	2.01866
H	-0.224838	1.958628	2.78283
H	0.735842	2.822978	1.59437
H	-0.511408	3.687987	2.50065
C	-4.295941	4.171552	-0.58524
H	-4.646310	4.114899	-1.61819
H	-5.160056	4.007666	0.06659



## SUPPORTING INFORMATION

H -3.933001 5.185461 -0.40240

**PtBu<sub>3</sub>**

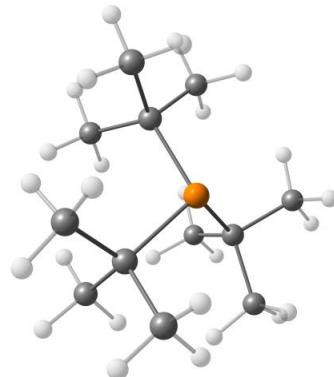
E: -814.887161986 a.u

ZPE: -814.515895 a.u

G: -814.556757 a.u

Cartesian coordinates:

P	-0.000167	0.000002	-0.71524
C	0.500697	1.714209	-0.00590
C	-0.653740	2.708902	-0.22065
C	0.919254	1.777634	1.46943
C	1.654484	2.244593	-0.88280
H	-1.015049	2.692807	-1.25223
H	-1.496305	2.535416	0.44838
H	-0.284556	3.720030	-0.01734
H	1.831215	1.213559	1.66767
H	1.120990	2.820295	1.74278
H	0.141590	1.406878	2.13818
H	1.872587	3.279808	-0.59611
H	2.576887	1.678386	-0.77429
H	1.376689	2.238321	-1.93983
C	-1.735097	-0.423477	-0.00584
C	-1.999173	-0.092941	1.46953
C	-2.771306	0.310491	-0.88280
C	-2.019391	-1.920560	-0.22073
H	-1.288704	-0.580567	2.13805
H	-1.967460	0.978885	1.66782
H	-3.002689	-0.440281	1.74314
H	-2.627501	0.072275	-1.93971
H	-3.776935	-0.017524	-0.59549
H	-2.741553	1.392445	-0.77505
H	-3.079754	-2.106219	-0.01781
H	-1.824528	-2.225483	-1.25225
H	-1.448316	-2.563664	0.44851
C	1.234250	-1.290675	-0.00595
C	2.672749	-0.788192	-0.22161
C	1.080936	-1.684621	1.46959
C	1.116465	-2.555294	-0.88248
H	2.838944	-0.467510	-1.25336
H	2.944222	0.028381	0.44707
H	3.363954	-1.613406	-0.01847
H	0.137170	-2.193371	1.66870
H	1.883896	-2.379785	1.74265
H	1.148297	-0.825580	2.13812
H	1.903932	-3.261750	-0.59570
H	0.164932	-3.070916	-0.77368
H	1.249781	-2.311883	-1.93959



## SUPPORTING INFORMATION

**B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**

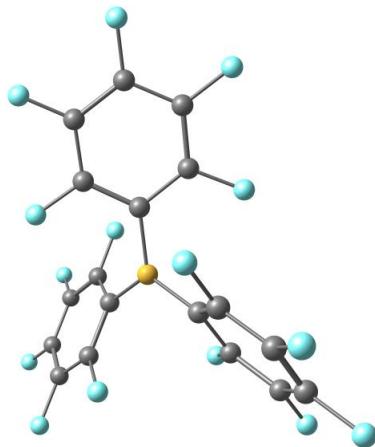
E: -2208.20959618 a.u

ZPE: -2208.053225 a.u

G: -2208.115161 a.u

Cartesian coordinates:

C -1.543048 -0.261918 -0.00034  
 C -2.420554 0.509617 -0.76001  
 C -3.785492 0.285595 -0.77954  
 C -4.314922 -0.732254 -0.00032  
 C -3.479370 -1.518529 0.77884  
 C -2.116965 -1.279719 0.75932  
 F -1.953683 1.491632 -1.53213  
 F -4.588072 1.029357 -1.52972  
 F -5.617968 -0.953351 -0.00027  
 F -3.991664 -2.485432 1.52898  
 F -1.352201 -2.052697 1.53143  
 B -0.000284 -0.000135 -0.00012  
 C 0.998053 -1.205149 0.00011  
 C 0.769494 -2.350674 -0.76007  
 C 1.646330 -3.420420 -0.77943  
 C 2.792039 -3.369896 0.00049  
 C 3.054319 -2.253327 0.78021  
 C 2.165976 -1.193105 0.76048  
 F -0.313952 -2.437437 -1.53281  
 F 1.404272 -4.487164 -1.53011  
 F 3.635364 -4.387552 0.00068  
 F 4.147343 -2.213386 1.53105  
 F 2.452279 -0.144418 1.53303  
 C 0.544376 1.466857 -0.00005  
 C 1.650636 1.841107 -0.76058  
 C 2.139295 3.135102 -0.78007  
 C 1.523379 4.102320 0.00008  
 C 0.425318 3.771713 0.78014  
 C -0.049339 2.472509 0.76051  
 F 2.266649 0.945813 -1.53358  
 F 3.184063 3.458400 -1.53108  
 F 1.983651 5.341263 0.00013  
 F -0.155048 4.698615 1.53121  
 F -1.100557 2.196546 1.53339



## SUPPORTING INFORMATION

**B(NO<sub>2</sub>-Mes)<sub>3</sub>**

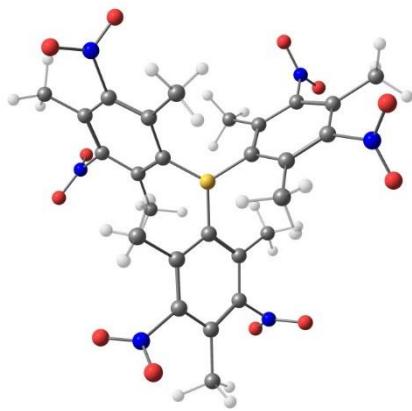
E: -2300.46393332 a.u

ZPE: -2299.918641 a.u

G: -2300.004024 a.u

Cartesian coordinates:

B -0.000039 0.000079 -0.00731  
 C 1.083401 1.147619 -0.005448  
 C 2.165003 1.099805 0.894375  
 C 3.093693 2.133288 0.860273  
 C 3.031201 3.226311 0.00993  
 C 1.942828 3.221735 -0.852524  
 C 0.970998 2.231048 -0.899521  
 C 0.452069 -1.511962 -0.005398  
 C -0.12964 -2.424653 0.894716  
 C 0.301008 -3.745706 0.860538  
 C 1.278265 -4.238205 0.009536  
 C 1.817883 -3.293359 -0.85333  
 C 1.446099 -1.956339 -0.899939  
 C -1.53558 0.364429 -0.00539  
 C -2.03528 1.324566 0.894713  
 C -3.394727 1.611984 0.860479  
 C -4.309812 1.011718 0.009573  
 C -3.761282 0.071917 -0.85314  
 C -2.417408 -0.274388 -0.899846  
 C 2.343963 -0.008512 1.905104  
 H 1.389651 -0.414596 2.2368  
 H 2.926695 -0.830257 1.481119  
 H 2.86546 0.345473 2.794989  
 C -0.135481 2.33207 -1.922948  
 H -0.479512 1.350212 -2.244333  
 H -0.993981 2.87171 -1.515862  
 H 0.194647 2.8631 -2.816412  
 C -1.164996 2.033213 1.905863  
 H -0.335165 1.410268 2.235909  
 H -0.745983 2.949743 1.482747  
 H -1.732034 2.305999 2.796495  
 C -1.951278 -1.283048 -1.92317  
 H -0.928533 -1.090455 -2.243421  
 H -1.990195 -2.296418 -1.516343  
 H -2.575346 -1.262148 -2.817222  
 C -1.178229 -2.025026 1.905995  
 H -1.053495 -0.994787 2.235673  
 H -2.181603 -2.120584 1.48325  
 H -1.13067 -2.652227 2.796818  
 C 2.086842 -1.048563 -1.923308  
 H 1.409172 -0.258689 -2.243579  
 H 2.984348 -0.576199 -1.516741  
 H 2.380326 -1.599686 -2.817391  
 C 1.701068 -5.680293 -0.014389  
 H 1.226688 -6.19239 -0.854078  
 H 2.781617 -5.765053 -0.14084  
 H 1.434498 -6.190874 0.908912  
 C 4.069083 4.313101 -0.013668  
 H 4.644306 4.336867 0.909834  
 H 4.749885 4.158006 -0.853215  
 H 3.602872 5.291568 -0.14005  
 C -5.770073 1.366606 -0.014506  
 H -6.079106 1.852356 0.908957  
 H -5.976143 2.033875 -0.85395  
 H -6.383749 0.473288 -0.141537  
 N 2.869602 -3.7564 -1.777744  
 O 3.994481 -3.351648 -1.576719  
 O 2.533398 -4.506295 -2.66957  
 N -0.335566 -4.698565 1.790262  
 O 0.28084 -4.996722 2.791856



## SUPPORTING INFORMATION

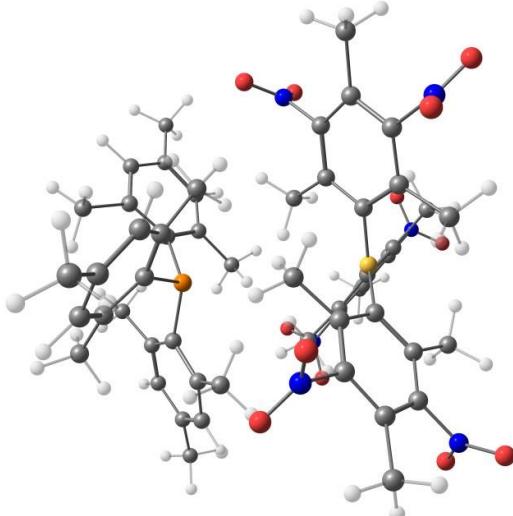
O -1.433682 -5.106229 1.482759  
 N 4.237972 2.058097 1.788996  
 O 5.14122 1.313444 1.478807  
 O 4.187543 2.738378 2.792349  
 N 1.817854 4.364491 -1.776387  
 O 0.904804 5.136096 -1.575018  
 O 2.635386 4.448729 -2.668171  
 N -4.688105 -0.607414 -1.777566  
 O -4.900102 -1.783931 -1.576461  
 O -5.169413 0.058711 -2.669395  
 N -3.901939 2.639903 1.789831  
 O -3.707647 3.794696 1.481126  
 O -4.46694 2.255343 2.792291

**PMes<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> encounter complex**

E: -3690.55038562 a.u  
 ZPE: -3689.474874 a.u  
 G: -3689.593395 a.u

## Cartesian coordinates:

C -1.334967 -1.507756 -3.45404  
 C -1.347718 -0.639569 -2.369501  
 B -2.257632 0.01129 -0.024144  
 C -2.251077 -0.899464 -1.31768  
 C -3.123452 -1.998617 -1.411122  
 C -2.258824 1.586858 -0.164464  
 C -3.126805 2.215649 -1.078047  
 C -3.048953 3.595233 -1.2108  
 C -2.183611 4.417377 -0.500704  
 C -1.371238 3.748841 0.403909  
 C -1.37166 2.371285 0.598455  
 C -3.036534 -2.813019 -2.533934  
 C -2.258525 -0.659583 1.408623  
 C -3.126693 -0.187042 2.41206  
 C -3.05332 -0.771432 3.669001  
 C -2.194589 -1.80534 4.019485  
 C -1.381638 -2.24957 2.986661  
 C -1.37521 -1.717436 1.701093  
 C -2.156954 -2.620404 -3.587496  
 P 2.799423 0.004093 0.019786  
 C 3.365926 -1.727505 0.245486  
 C 2.672156 -2.694354 -0.51872  
 C 4.253717 -2.164287 1.248135  
 C 2.782086 -4.040185 -0.191052  
 C 4.313656 -3.524422 1.550835  
 C 3.56252 -4.474932 0.873981  
 H 2.229852 -4.768194 -0.778753  
 H 4.981625 -3.848941 2.343762  
 C 3.401151 0.681304 -1.57722  
 C 2.704266 1.816267 -2.052869  
 C 4.329294 0.048655 -2.427253  
 C 2.857666 2.214888 -3.375177  
 C 4.433992 0.47676 -3.750451  
 C 3.686533 1.530797 -4.256721  
 H 2.304567 3.081112 -3.727412  
 H 5.136256 -0.032057 -4.404781  
 C 3.351961 1.055898 1.419911  
 C 2.629834 0.886901 2.62413  
 C 4.261161 2.127138 1.318356  
 C 2.738021 1.837448 3.631933  
 C 4.318737 3.063729 2.35015  
 C 3.543896 2.961893 3.496956  
 H 2.164956 1.699167 4.544536  
 H 5.004812 3.90027 2.251634  
 C -0.40226 1.761347 1.576504  
 H -0.885377 1.560708 2.535833



## SUPPORTING INFORMATION

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H -0.002737 0.82416 1.193149  
H 0.456128 2.403057 1.770849  
C 5.232707 2.304389 0.176962  
H 5.622069 1.348992 -0.176926  
H 4.785397 2.80255 -0.686442  
H 6.077939 2.910122 0.50906  
C 1.788741 -0.333871 2.892253  
H 1.044089 -0.141994 3.666838  
H 1.274445 -0.682061 1.995999  
H 2.408258 -1.169681 3.230695  
C 3.561643 4.03376 4.552145  
H 2.736793 4.73469 4.388953  
H 3.443301 3.610969 5.552381  
H 4.492698 4.603646 4.527514  
C -2.186707 5.909547 -0.685347  
H -2.21603 6.162507 -1.747065  
H -3.075661 6.338224 -0.21818  
H -1.300349 6.372583 -0.258961  
C -4.147814 1.455287 -1.890398  
H -3.732291 1.1545 -2.855202  
H -4.48415 0.55626 -1.3762  
H -5.032502 2.062798 -2.085718  
C -0.373475 0.507878 -2.315584  
H 0.023492 0.630077 -1.308957  
H 0.484348 0.362105 -2.969989  
H -0.853442 1.444085 -2.610205  
C -4.151481 -2.32521 -0.354204  
H -3.742131 -3.019477 0.384302  
H -4.486856 -1.435267 0.175866  
H -5.035713 -2.788391 -0.794332  
C -2.079538 -3.550851 -4.765758  
H -1.241697 -4.23993 -4.642233  
H -2.997139 -4.125522 -4.878607  
H -1.918594 -2.996754 -5.691513  
C 1.859694 -2.327495 -1.7334  
H 1.128267 -3.10189 -1.971165  
H 1.333155 -1.381352 -1.604495  
H 2.502176 -2.201406 -2.610156  
C 3.577357 -5.922176 1.283571  
H 2.734864 -6.131343 1.950487  
H 3.486379 -6.582867 0.418453  
H 4.495476 -6.177558 1.816549  
C 5.199847 -1.253938 1.992737  
H 5.588697 -0.460624 1.353326  
H 4.731138 -0.766587 2.851017  
H 6.047275 -1.834284 2.362586  
C 1.847474 2.669368 -1.154  
H 1.122673 3.249301 -1.728062  
H 1.308764 2.075446 -0.415312  
H 2.459734 3.377195 -0.587133  
C 5.273667 -1.041377 -1.982315  
H 5.632004 -0.877937 -0.965229  
H 4.814133 -2.032532 -1.999239  
H 6.140585 -1.065581 -2.645251  
C 3.758549 1.91586 -5.70908  
H 4.698122 1.592914 -6.161986  
H 2.941069 1.444805 -6.264106  
H 3.667147 2.996498 -5.840039  
C -4.143806 0.902108 2.16726  
H -3.726514 1.884562 2.401331  
H -4.476014 0.918318 1.130433  
H -5.030796 0.762902 2.786832  
C -2.204526 -2.402199 5.399456  
H -2.212403 -1.613947 6.155076  
H -3.107187 -3.000978 5.536566  
H -1.33122 -3.024309 5.578608  
C -0.399579 -2.252427 0.685817

## SUPPORTING INFORMATION

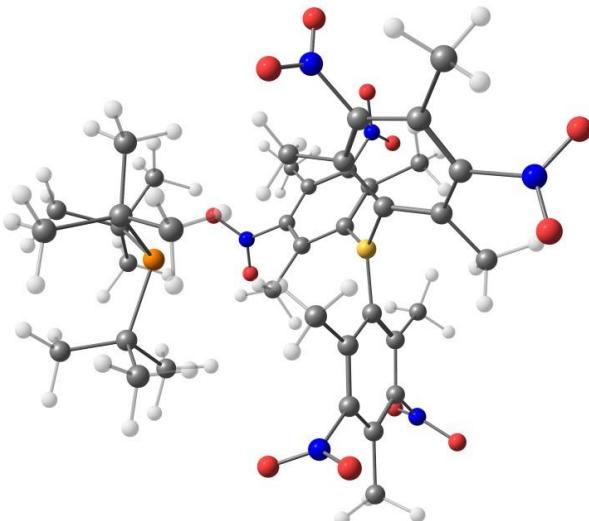
H -0.875347 -2.98496 0.029356  
H -0.001574 -1.448489 0.069339  
H 0.459117 -2.737196 1.148532  
N -3.93861 -0.251012 4.727934  
N -0.459357 -3.36677 3.269467  
N -3.929587 -3.985956 -2.599018  
N -0.44274 4.555341 1.220115  
N -3.936431 4.248511 -2.191356  
N -0.382202 -1.247945 -4.549888  
O -3.68833 0.855227 5.156706  
O -4.850685 -0.962791 5.09214  
O -0.708366 -4.428296 2.741156  
O 0.480729 -3.147851 4.005914  
O -0.546274 -0.237154 -5.198803  
O 0.493509 -2.068499 -4.731761  
O -4.93133 -3.890022 -3.276966  
O -3.594185 -4.959807 -1.961243  
O 0.50385 5.0655 0.656411  
O -0.693497 4.648826 2.401731  
O -3.691782 4.059005 -3.363744  
O -4.84471 4.924928 -1.757069

**PtBu<sub>3</sub>/B(NO<sub>2</sub>-Mes)<sub>3</sub> encounter complex**

E: -3115.37819141 a.u  
ZPE: -3114.459988 a.u  
G: -3114.563741 a.u

## Cartesian coordinates:

C -0.193199 -1.632961 -3.361217  
C -0.396104 -0.706234 -2.346069  
B -1.585246 -0.057146 -0.130244  
C -1.412776 -0.974843 -1.403714  
C -2.220323 -2.115298 -1.557562  
C -1.629082 1.513634 -0.285208  
C -2.460184 2.09663 -1.259538  
C -2.39122 3.471228 -1.444105  
C -1.547386 4.32103 -0.743591  
C -0.766395 3.69418 0.217006  
C -0.781667 2.331285 0.490303  
C -1.956967 -2.971056 -2.620337  
C -1.671695 -0.708907 1.305728  
C -2.657436 -0.276748 2.212552  
C -2.633031 -0.789305 3.502959  
C -1.694893 -1.695664 3.975453  
C -0.761993 -2.103161 3.03256  
C -0.718397 -1.664485 1.714236  
C -0.944633 -2.787528 -3.547578  
P 3.525567 0.146844 0.268615  
C 0.129022 1.765469 1.551147  
H -0.447851 1.313107 2.358207  
H 0.796262 1.00489 1.135535  
H 0.760099 2.527085 2.003896  
C -1.524413 5.804949 -0.982101  
H -1.622693 6.029725 -2.045144  
H -2.360675 6.277627 -0.46265  
H -0.594674 6.251261 -0.634054  
C -3.425676 1.288578 -2.092855  
H -2.971762 1.00443 -3.045182  
H -3.73715 0.377245 -1.584977  
H -4.330027 1.857312 -2.315033  
C 0.493708 0.505815 -2.233804  
H 0.98472 0.544346 -1.258062  
H 1.277658 0.514465 -2.986216  
H -0.080071 1.422978 -2.369899  
C -3.35559 -2.448543 -0.619723  
H -3.019474 -3.123985 0.171116



## SUPPORTING INFORMATION

H -3.768676 -1.559699 -0.146063  
H -4.173361 -2.938182 -1.15111  
C -0.653689 -3.765123 -4.651702  
H 0.198536 -4.390932 -4.378692  
H -1.51079 -4.403839 -4.856281  
H -0.401626 -3.242792 -5.57603  
C -3.742488 0.700492 1.829057  
H -3.454683 1.721863 2.088981  
H -3.953605 0.672581 0.761431  
H -4.676597 0.4784 2.347587  
C -1.726036 -2.222858 5.382713  
H -1.995137 -1.434751 6.087509  
H -2.47363 -3.014478 5.466305  
H -0.757427 -2.61855 5.682696  
C 0.355016 -2.176503 0.78688  
H -0.079844 -2.743982 -0.036525  
H 0.942722 -1.354992 0.368217  
H 1.053447 -2.840623 1.290867  
N -3.659452 -0.32858 4.456196  
N 0.251248 -3.078886 3.479608  
N -2.792536 -4.180189 -2.749934  
N 0.142479 4.554885 0.999121  
N -3.253949 4.08114 -2.472608  
N 0.898444 -1.405778 -4.32803  
O -3.595891 0.826845 4.818381  
O -4.491103 -1.137764 4.80895  
O 0.054501 -4.241921 3.206287  
O 1.204252 -2.64541 4.094393  
O 0.753683 -0.5135 -5.135344  
O 1.860538 -2.141932 -4.252706  
O -3.674679 -4.162694 -3.582583  
O -2.53549 -5.101075 -2.005869  
O 1.194479 4.866018 0.478863  
O -0.230152 4.893629 2.100241  
O -2.998784 3.822545 -3.629527  
O -4.154347 4.79666 -2.087735  
C 4.357018 -0.99808 -1.027592  
C 4.265594 -0.377889 -2.43246  
C 5.82437 -1.374572 -0.778466  
C 3.498063 -2.278145 -1.098142  
H 3.246685 -0.078098 -2.678095  
H 4.923425 0.479461 -2.569378  
H 4.556453 -1.135276 -3.166921  
H 5.961524 -1.956162 0.132723  
H 6.181929 -1.991421 -1.610952  
H 6.469231 -0.496877 -0.719172  
H 3.904994 -2.940923 -1.868979  
H 3.471291 -2.836408 -0.164392  
H 2.469836 -2.042279 -1.386661  
C 4.178569 1.927333 -0.021454  
C 3.878887 2.813306 1.200083  
C 5.67079 2.071751 -0.352183  
C 3.335694 2.527186 -1.166472  
H 2.830364 2.757491 1.494169  
H 4.498212 2.579637 2.065141  
H 4.073597 3.855673 0.929534  
H 5.940219 1.596888 -1.295294  
H 5.914998 3.136091 -0.446627  
H 6.308357 1.656407 0.42917  
H 3.64348 3.565315 -1.330094  
H 3.446001 1.999212 -2.111602  
H 2.274723 2.545204 -0.902698  
C 4.117582 -0.413696 2.005534  
C 3.992272 -1.94007 2.15109  
C 5.54577 -0.021363 2.409552  
C 3.112998 0.169307 3.021657  
H 2.997556 -2.293636 1.879211

**SUPPORTING INFORMATION**

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H 4.730577 -2.491038 1.569867  
H 4.141362 -2.202017 3.203156  
H 5.681348 1.057349 2.482529  
H 5.766005 -0.440898 3.397912  
H 6.291314 -0.409357 1.714267  
H 3.383488 -0.170167 4.027054  
H 3.091124 1.257173 3.036714  
H 2.100775 -0.192981 2.821893

## SUPPORTING INFORMATION

## 10. References

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